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ESR OF BITUMENS: TEMPERATURE DEPENDENCE STUDIES.

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Introduction

Electron spin resonance (ESR) provides a convenient method for the structural elucidation of complex macromolecules. It may, therefore, be utilized as a probe in the exploration of the micro-environment within large molecules, without the danger of either chemical decomposition, physical deformation, or dissolution from a solvent system. For bituminous materials (1,2), two different sources of ESR absorption are expected: that resulting from the presence of free radicals, and that arising from vanadium chelates. Considerable efforts have been directed toward the investigation of the latter; viz., nitrogen superhyperfine splittings due to the inherent paramagnetic vanadium moieties (3), the isotropy-anisotropy nature of vanadium (4), the ligand types of vanadium complexes (5), spectral parameters from petroporphyrins (6), vanadium chelate model systems (7,8,9,10), calculation (11), and synthesis (12) of anisotropic vanadium spectra in asphaltenes, and the enhancement and separation of vanadium signals (13,14) have been studied. Conversely, little research into the nature of free radical bitumens has been completed, with the exception of work performed concerning spin concentrations (15) and relaxation times (16), and examination of the ESR spectra of various gel permeation chromatography fractions of bitumens (17). Only recently have the g -values of a large variety of bituminous materials been collected and correlated with their structural properties (1).

It has been previously concluded (15,3) that the free radical in bitumens is located in a large aromatic ring system in such a manner as to optimize its stabilization by resonance of the delocalized π -electron. g -Value studies further reveal that these free spins resemble neither the semiquinone-quinone system (L- or H-forms of carbon) nor any other localized, heteroatom-bearing radical. Since both spin numbers (N_g) and g -values have been correlated with structural differences (2) and other physical properties of bitumens (15), basic investigation into the area of spin correlation or spin excitation will reveal information about the nature of the spins, especially regarding their interactions with their nearby host, the condensed aromatic systems. Information concerning the transfer and mobility of the spin and charged particles is essential to an understanding of the chemistry of bitumens.

Naturally occurring bituminous materials fall into two categories: the bitumens (including petroleum compounds) and the pyrobitumens. The former may be further subdivided into mineral waxes, asphalts, and asphaltides, and the pyrobitumens into asphaltoids and coals. These materials may be fractionated on the basis of solubility characteristics in various common solvents. Thus, resins are defined as n -pentane soluble, propane insoluble fractions; asphaltenes as benzene soluble, n -pentane insoluble fractions, carbenes as carbon disulfide soluble, benzene insoluble fractions, and carboids as the carbon disulfide insoluble fractions. The sequential progression from resin to carboid is associated with an increase in macromolecular size. These bitumens are characterized by condensed aromatic nuclei associated either intra- or intermolecularly and substituted with aliphatic or naphthenic substituents at their peripheries.

Previously, investigations into the dependence of certain physical properties of bitumens on temperature have yielded valuable information. Hence, methylene rocking-vibrational bands arising from paraffinic groups (18), measurements of gap energy (19), magnetic susceptibility (6) as affected by odd numbers of nitrogen ligands, and vanadium

51 nuclear-spin interaction in states of molecular association or dissociation with the bitumen matrix (4), are all temperature dependent. The present study will investigate the nature of the dependence of the ESR signal intensity with temperature in bitumen samples. The relative intensity of ESR spectra bands is expected to yield fairly high precision, if the detection systems are provided with suitable modulation amplitude and utilized at correct power levels (i.e., not causing saturation). It is anticipated that further information concerning the nature of the free radicals in bituminous materials, especially those under excited conditions, will be obtained. However, the immediate objective of this paper is to find whether there are any spins that are thermally accessible (e.g., singlet to triplet transitions); if so, then the fate of the doublet spins is examined. The next question that should be considered is the effect that is exerted on the spins by the host (stacked aromatic discs) in the micro environment.

Data Treatment

In the study of the variation of ESR intensity with temperature (20), two types of dependence are usually found. When there is negligible interaction between the adjacent spins, and the free radical behaves as a paramagnetic molecule (with 1/2 spin per molecule), as in the case of the Banfield and Kenyon's radical for example, then the Curie-Weiss law is followed and the intensity (I) expressed as that of a doublet state,

$$I_d = xN_d w/2kT \dots \dots \dots (1)$$

where x is a constant, N, the particle number of the doublet type, w, the energy level being split by the magnetic field, k, the Boltzmann constant and T, the absolute temperature. On the other hand, if there is significant interaction between the unpaired electrons, the fourfold level will be split into a diamagnetic singlet state (spins anti-parallel) and a magnetic triplet state (spins parallel). In this particular case, the temperature dependence is exponential and the ground state is a singlet. Consequently, the triplet state will lie at an energy J, above the ground level. In this case,

$$I_{st} = 2xN_{st} w/kT \exp \left[\frac{J}{kT} + 3 \right] \dots \dots \dots (2)$$

where N is the particle number of the singlet-triplet transition. For simplicity, the abbreviation,

$$E = \left[\exp \left(\frac{J}{kT} \right) + 3 \right]^{-1} \dots \dots \dots (3)$$

will be used.

Assuming that both temperature dependent processes, of spin-spin interactions and non-interaction, are operative within the system, then

$$I = I_d + I_{st} = c/T + aE/T \dots \dots \dots (4)$$

where c and a are constants. Their ratio is an indication of the number of doublet spins to that of the singlet-triplet spins. The fraction of doublet spins can thus be evaluated, e.g.,

$$\frac{N_d}{N_d + N_{st}} = 4c/(a+4c) \dots \dots \dots (5)$$

J, for a given sample may be determined as follows: a set of calibration curves is prepared (Fig. 1) by plotting the normalized E values, E_N, vs. T in which J is varied from 0.02 to 0.12 eV in 0.1 eV increments. The function is then normalized by setting E=0 at 123°K and E=1 at 400°K, so that

$$E_N = (E - E_{123}) / (E_{400} - E_{123}) \dots \dots \dots (6)$$

The raw intensity data are treated by plotting $(IT)_N$ vs. T. The normalization expression is similar to Equation 6

$$(IT)_N = \left[IT - (IT)_{123} \right] / \left[(IT)_{400} - (IT)_{123} \right] \dots \dots \dots (7)$$

In this manner, J is estimated by matching the normalized data curves $(IT)_N$ vs. T with the calibration curves having predetermined J values. This E_N vs. T curve is then vertically shifted by the addition of a constant quantity, $c' = (IT)_{123} / \left[(IT)_{400} - (IT)_{123} \right]$ to E_N , as in Fig. 2. Finally, point by point, the quantity, $E_{N+c'}$, is multiplied by $\left[(IT)_{400} - (IT)_{123} \right] / T$, to obtain I, so that,

$$I = (E_{N+c'}) \left[(IT)_{400} - (IT)_{123} \right] / T \dots \dots \dots (8)$$

Subsequently, the curve I vs. T is plotted (Fig. 3), allowing the individual components to be constructed from the following:

$$a = \left[(IT)_{400} - (IT)_{123} \right] / (E_{400} - E_{123}) \dots \dots \dots (9)$$

$$c = (IT)_{123} - a E_{123} \dots \dots \dots (10)$$

It is evident that, when IT is plotted vs. T, the quantity c is constant, shifting the curve in a direction parallel to the y-axis toward the experimental points (refer to Equation 4).

Results

Results obtained from the asphaltene fraction of four different crude oils and phthalocyanine are listed in Table I. Data from a number of charge-transfer complexes were used as an internal check of the validity of this treatment. The J-values obtained for both $NH_4^+TCNQ_2^-$ and Na^+TCNE^- complexes, according to the present graphic methods, are in excellent agreement with published results. For the chloranil-diaminodurene complex, however, $J=0.15$ fits more appropriately in the low temperature range and $J=0.25$ fits more appropriately in the high temperature range. All doublet concentrations agree well with published results for the low temperature range (Table I). No published result is available for $NH_4^+TCNQ_2^-$, although the doublet concentration for this compound is anticipated to be nil.

Table I PARAMETERS OF SPIN EXCITATION
FROM TEMPERATURE DEPENDENCE

| No. | Sample | J (eV) x 10 | $a \times 10$ | c | $N_d / (N_d + N_{st})$ (%) |
|----------------|------------------|--------------|---------------|-----------|----------------------------|
| a [#] | Mara* | 5.2 | 1.7 | 180 | 30 |
| b | Ragusa* | 9.5 | 5.3 | 120 | 8.0 |
| c | Wafra* | 9.0 | 5.0 | 100 | 7.6 |
| d | Baxterville* | 8.8 | 4.9 | 89 | 6.7 |
| e | Phthalocyanine | 8.0 | 2.4 | 220 | 27 |
| f | $NH_4^+TCNQ_2^-$ | 3.4 | 2.4 | -19 | -- |
| g | Na^+TCNE^- | 25 (16)** | 450.0 -- | 83 -- | 0.07 (0.03) |
| h | Chloranil-DAD | 15 (16) | 32.0 -- | 4.1 -- | 0.04 (0.04) |
| | | 20 | 130.0 | 4.1 | 0.01 |
| | | 25 | 560.0 | 4.1 | 0.003 |
| i | Etioporphyrin II | 2.7 | 2.3 | -21 | -- |

#Identification of the lower case alphabets see curves in Fig. 4.

*Asphaltene

##TCNQ, 7,7,8,8-Tetracyano-p-quinodimethan; TCNE, Tetracyanoethylene; DAD, Diaminodurene.

**Quantities in parentheses are literature values.

The computed curves of the bitumen sample and phthalocyanine, match favorably with the experimental data points as can be seen from Fig. 4. It is evident that two different trends occur. The upper two samples (a and e) form a different trend than those of the lower three asphaltenes (b,c,d). These differences might very well be attributed to the constants, a and c, and may not result from the J-values.

In order to correlate the J values obtained from ESR, with those from magnetic susceptibility measurements, the corrected magnetic susceptibility (6) of an enriched petroporphyrin fraction from Boscan crude was treated, and a J value of 0.033 eV gave a perfect fitting (Fig. 5). However, the J value obtained by ESR measurement of the pure etioporphyrin II, is 0.027 eV. This indicates that there is fair agreement. So far, the lowest J value is, among asphaltenes, that of Mara (J=0.025 eV), which contains the highest amount of porphyrin (21). The fact that the J value of phthalocyanine is higher has not been accounted for, but it is suggested that contaminants, such as dimeric or polymeric species, may affect the energy separation.

Finally, in order to check the validity of the assumption that asphaltene exhibits singlet-triplet transitions, which typify many known charge-transfer complexes, e.g., TCNQ triethylammonium salt, a log-log plot, as in Fig. 6, was constructed for an asphaltene sample and a TCNQ complex. In Fig. 6, the points were obtained from experimental IT data, while the curves were computed from the J value of $4/(e^{J/kT}+3)$. The coincidence of the experimental points with the computed curves, together with the specific shape of the curve, suggests that asphaltenes exhibit singlet-triplet excitations.

Discussion

Condensed-ring aromatic molecules are disk-like in shape, and, not surprisingly, tend to orient themselves into crystallites of stacks or chains. Highly oriented, organic, free radicals are of significant interest, since the paramagnetism of the system is dominated by the presence of a strong antiferromagnetic exchange interaction directed axially through the center of the disks (Heisenberg chain) (22). This one-dimensional array of stacked, exchange-coupled, planar molecules, each with a spin of 1/2, can exhibit a spin of either one (doublet) or two (singlet-triplet) per repeating unit.

The layer diameter (La) of most bitumen aromatic crystallite sheets is approximately 8.5-15 Å, the cluster diameter (Lc) being within the range of 16-20 Å. The charge-transfer process in asphaltics is favored by the motion of electrons or holes axially to the plane of the disks (23). Infrared evidence suggests that these disks are held in stack formation by $\pi-\pi$ associations of the donor-acceptor type (24). Hence, it is possible that excitation processes such as those manifested by some known donor-acceptor charge-transfer complexes could exist (Table II).

Table II LOW-LYING SINGLET-TRIPLET ENERGY INTERVALS AND ACTIVATION ENERGIES FOR CONDUCTION OF SOME CHARGE-TRANSFER COMPLEXES IN eV

| Complex | J | $\Delta\epsilon$ | Ref. |
|--|-------|------------------|------|
| $\text{NH}_4^+\text{TCNQ}_2^-$ | 0.034 | 0.14 | 32 |
| $3\text{AsMe}^+\text{TCNQ}_2^-$ | 0.065 | 0.30 | 34 |
| 4-Cyano-N-methyl-quinolium TCNQ_2^- | 0.018 | 0.08 | 34 |
| K TCNQ | 0.2 | 0.35 | 34 |
| p-Chloranil-DAD | 0.15 | 0.25 | 33 |

Table II LOW-LYING SINGLET-TRIPLET ENERGY INTERVALS
AND ACTIVATION ENERGIES FOR CONDUCTION
OF SOME CHARGE-TRANSFER COMPLEXES IN eV (cont.)

| <u>Complex</u> | <u>J</u> | <u>$\Delta\epsilon$</u> | <u>Ref.</u> |
|---|----------|------------------------------------|-------------|
| p-Chloranil-p PDA* | 0.13 | 0.43 | 35 |
| TMPD ⁺ ClO ₄ ^{-**} | 0.0305 | -- | 36 |

*p-Phenylenediamine

**N,N,N',N',-Tetramethyl-p-phenylenediamine

Treatment of spin excitation in petroleum asphaltenes indicates that excitons may be raised from the ground singlet state to a thermally accessible triplet state, in addition to the usual doublet state. Furthermore, there is an apparent lack of spatial correlation; probably due to the random orientation of the crystallites in the mesomorphic medium. This independent, delocalized spin excitation may be accounted for by Wannier spin excitons rather than the Frenkel excitons, the latter being characterized by TCNQ radical ions, or Wurster's blue perchlorates (25).

The fact that the doublet concentration in phthalocyanine, as well as in Mara asphaltene (V=2370 ppm., highest vanadium content), is higher than those of the remaining samples suggests that paramagnetic impurities may inhibit the spin excitation. The four-fold difference in doublet concentration between high-vanadium and low-vanadium samples may indicate certain degrees of localization due to nuclei-spin interaction. In addition, the excitons inherent in bituminous materials are not associated with paramagnetic metal complexes. However, the gap energy of high-vanadium bitumens is generally small, suggesting that potential electron donors, such as heteroatom centers, may be present in these bituminous structures.

The Russell effect (thermal luminescence) has been observed in metal-free asphaltene and resin fractions of bitumens (26). Specifically, strong infrared luminescence and reflectance (27) were observed for coal-hydrogenated and benzene-suspended asphaltenes. It is doubtful that, as reported earlier (27), this type of luminescence may be attributed to the presence of polynuclear aromatic hydrocarbons alone. It is possible that charge-transfer complexes play a significant role.

The enhancement of the asphaltene ESR signal was observed during the course of intra muros electrolytic redox experiments. It is possible that excitons are also responsible for this type of reaction. Other observations of asphaltenes, such as the ease of induction of the Overhauser effect (proton polarization enhancement) (28), the Seebach effect (29) and charge-transfer nature in the presence of polar solvents (38) may be accounted for by exciton behavior. Charge carriers observed in electronic resistivity studies may also be of exciton origin.

The selection of phthalocyanine and etioporphyrin as model compounds in this experiment is based on the fact that both compounds exhibit exciton behavior. It is known that both compounds, when arranged in stacks, have an overall structure similar to those of crystallites in bitumens with approximately the same interplanar distances ($d=3.4$ Å). ESR signals, close to $g=2$, have been detected in metal free α - and β -phases of phthalocyanine (30); the nature of these radicals is most likely due to spin excitations. Recently, it has been noted that porphyrins exhibit chemoluminescence, the energy transfer of such excitation being demonstrated by the decomposition of tetralin peroxide (31).

The small differences in J-values and doublet concentration among the remaining asphaltenes, excluding the high vanadium-containing sample, (Mara) indicates that these parameters are perhaps constant, within the range of experimental error. However, a careful examination of the parameters reveals that both (last two columns, Table III)

vary proportionally with each other, and inversely with aromaticity values (Table III). This trend also agrees with the electronic conductivity of native asphaltene (Room temperature resistivity ρ_{25} and $\Delta\epsilon$ are listed for a number of asphaltenes) (Table III). Considering the above, the nature of the charged particles within bitumens are influenced by their interaction with the polyaromatic systems present.

Table III RESISTIVITY PARAMETERS AND AROMATICITY
OF ASPHALTENES

| Asphaltene | f_a^* | $\rho_{25} \times 10^{-15}^{**}$ (ohm-cm) | $\Delta\epsilon^{**}$ (eV) | $J \times 10^2$ (eV) | $N_d / (N_d + st)$ (%) |
|-------------|---------|--|-------------------------------|-------------------------|---------------------------|
| Baxterville | 0.53 | 3.1 | 1.2 | 8.8 | 6.7 |
| Laquillas | 0.41 | 590 | 1.5 | -- | -- |
| Wafra | 0.37 | 10000 | 1.7 | 9.0 | 7.6 |
| Ragusa | 0.26 | -- | -- | 9.5 | 8.0 |

*Ref. 37

**Ref. 19

In order to further understand the nature of the singlet species within the bitumens, photoexcitation experiments should be conducted with these samples. Due to the interference of the vanadium hyperfine absorptions, ENDOR would prove to be an excellent tool for this work. The location of the $\Delta_m = \pm 1$ and $\Delta_m = \pm 2$ lines and of zero-field splitting parameters will be reported in a subsequent paper.

Experimental

A Varian V 4502 x-band spectrometer equipped with a 12 in. V 4013 A magnet and a V 4532 dual cavity (100 KHz modulation at sample and 400 Hz at reference) was employed. The temperature level in the range between 123° and 400°K was precalibrated and held within $\pm 3^\circ$ by use of a Varian variable temperature accessory. The relative intensity of the free radical absorption was reproducible in repeated trials to within 4%. Raw data of the intensity together with the corresponding temperature for the bitumens and phthalocyanine can be located as points in Fig. 4.

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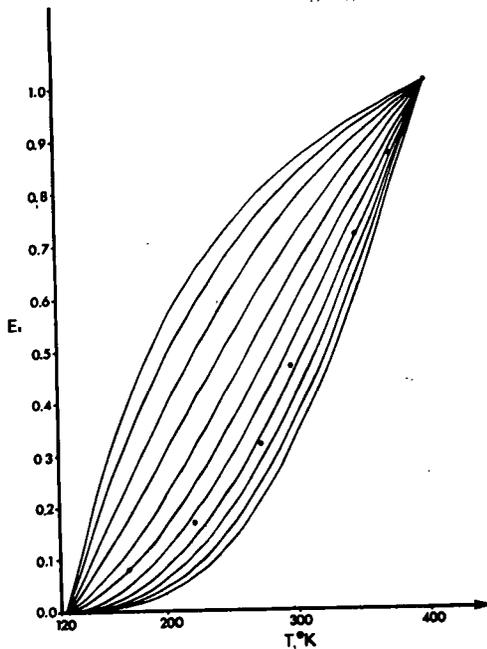


Fig. 1. A series of calibration curves of the general type, $E = \exp(JkT + 3)^{-1}$ with known values for J . (E is normalized so that $E_{123^{\circ}K} = 0$ and $E_{400^{\circ}K} = 1$. From left to right, J increases from 0.02 eV to 0.12 eV with 0.01 eV increments. The points indicate the values for the Baxterville asphaltene, $J = 0.088$ eV).

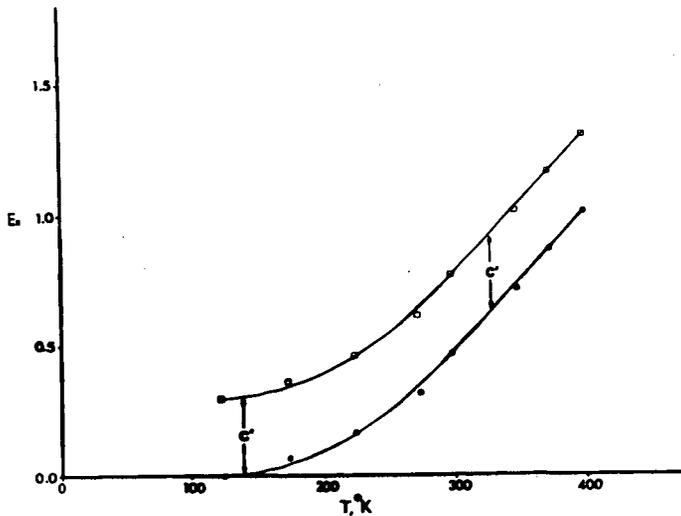


Fig. 2. Graphical Matching Procedure of the Baxterville Asphaltene: The lower line represents $(E - E_{123}) / (E_{400} - E_{123})$; the upper line indicates that the lower line has been shifted up by an amount of c' , where $c' = 0.292$.

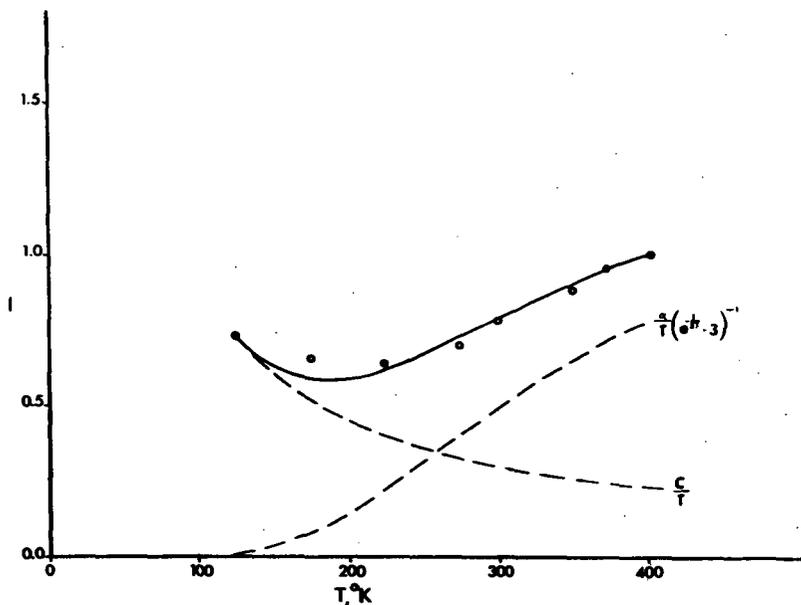


Fig. 3. Two Components for a Baxterville Asphaltene. (The circles indicate experimental data. The continuous line represents a theoretical curve with $J=0.088$, $c=89$, $a=4900$. The C/T curve is the doublet contribution; the E/T curve is singlet-triplet contribution).

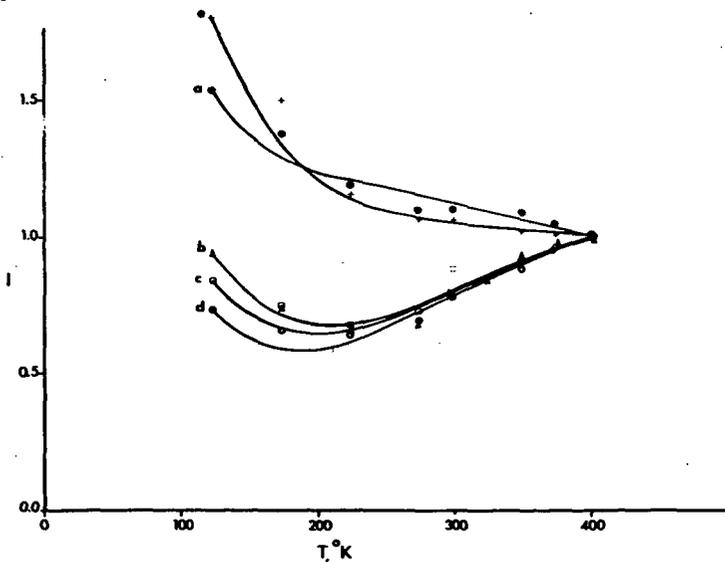


Fig. 4. Intensity Data of Asphaltenes (see Table I for sample identification).

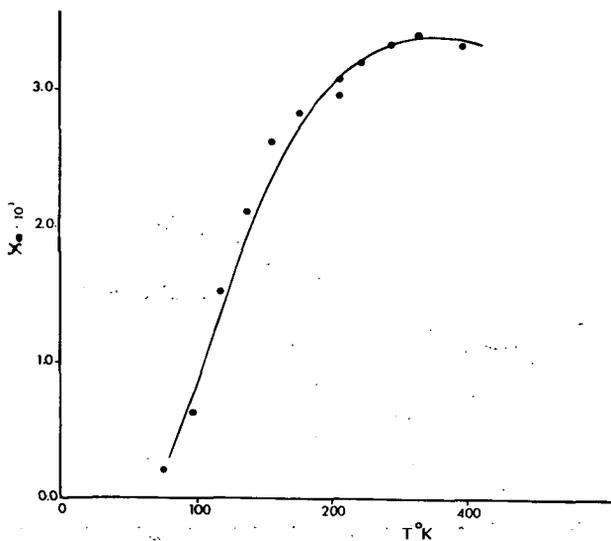


Fig. 5. Magnetic Susceptibility of a Boscan Petroporphyrin (J is approximately 0.038 eV).

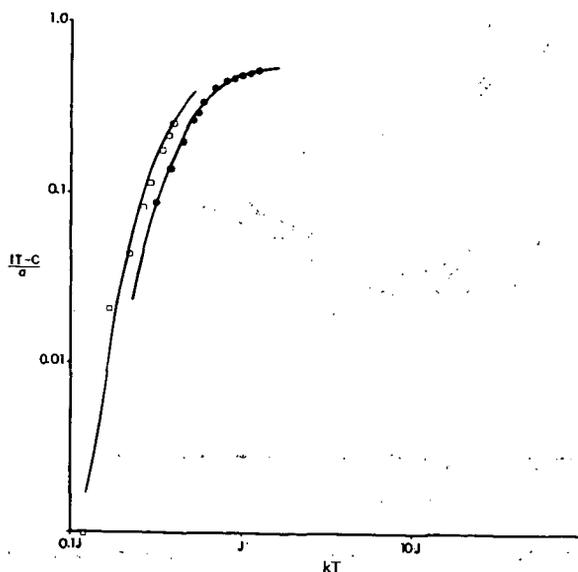


Fig. 6. Double Log Plot of $4E$ vs. kT for a TCNQ Salt (round) and a Baxterville Asphaltene (square). Curves are computed with known J values obtained by graphical procedure. The points are obtained from experimental IT data, i.e., the y-axis can be plotted as $(IT-c)/a$.