ELECTRON SPIN RESONANCE OF PETROLEUM ASPHALTICS

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Introduction

A considerable body of information about the Electron Spin Resonance (ESR) properties of petroleum asphaltenes has developed during the past few years. Among the basic parameters obtained by ESR measurements are N_g, the number of unpaired spins per gram of material; $|A|$, the electron-nuclear spin coupling constant; and g, the effective Landé g-factor for the unpaired electron spins. A review of what is already known, and the addition of new data may both clarify the present state of understanding of asphaltene ESR and stimulate further research in this area. The ESR studies briefly considered here may be divided into two parts: (1) measurements of the free radical absorption, and (2) measurements of the ESR absorptions due to naturally occurring vanadium and synthetic vanadium chelates.

Nature of Free Radical

The asphaltic fraction of petroleum has been found to yield a single ESR resonance near a g-value of 2.00[1,2,3]. For most asphaltics the line shape is between Lorentzian and Gaussian. The inhomogeneous broadening characteristics indicate that, in addition to dipolar interactions, the magnetic electron interacts with hydrogen or other nuclei to produce multiplet line structures. The apparent absence of fine structures in the radical absorption appears to be the result of a superposition of many such multiplets. The g-values of most asphaltics fall in the narrow range of 2.0027-2.0036. The differences between measured g-values and the g-value of a free electron (g_e), $|g - g_e|$, are shown in Fig. 1 for six native asphaltenes and a variety of other types of free radicals. It may be deduced that the unpaired spins in asphaltene do not appear to belong to the semiquinone or the radical ion families. However, they are close to neutral radicals, in contrast to the radicals in coals and L-forms of carbons which are semiquinones[1].

Intensity measurements are usually troublesome, but when properly done with suitable modulation amplitude and correct power levels (not causing saturation), the spin concentration, N_g, can be used as a basis for differentiating or classifying different asphaltic samples. Figure 2 displays the N_g data for 11 native asphaltenes from different sources: 2 native gilsonite asphaltenes, 3 refinery asphaltenes, 5 heat-treated asphaltenes[4], 3 carbenes, 4 cokes and one lithium-reduced asphaltene. Aromaticity, f_a, as obtained from x-ray analysis[5] for these materials is apparently linearly related to log N_g. These data indicate that the free radical sites of these materials are associated with the aromatic moities of the asphaltic skeleton. Present findings confirm the previous observation[1] that different families of carbonaceous substances, e.g., asphaltenes, resins[6], coals, and carbons, show a characteristic slope and intercept when their f_a values are plotted against log N_g.

No effects on N_g were observed due to the action of light, oxygen or solvents; however, these factors do affect the spin-lattice relaxation time[7]. The free radical species of asphaltics are stable, in contrast to coal hydrogenation asphaltene[8]. Further, it was found[1] that the color intensity of asphaltics, i.e., the integrated intensity obtained by absorption spectrometry over the 600-800 mμ region also increases with the ESR intensity (Fig. 3). These data indicate that the free radical is stabilized by the resonance of the delocalized π-system in the asphaltic structure.

Vanadium Unpaired Spin

Most asphaltics contain vanadium in concentrations ranging from 6000 to less than 1 ppm. Common valence states of vanadium are +2, +3, +4, and +5. The +5 state is diamagnetic. The +3 state, although paramagnetic, is usually not observable by ESR due to internal electric field effects. Both the +2 and the +4 states can, however, be detected at room temperature. In contrast to oxovanadium (IV), V^{+2} is unstable and easily oxidized. The +4 state requires a non-cubic field for ESR observability, and this is fulfilled by the oxovanadium (IV) VO^{+2} type complexes[9]. The vanadium 51 nucleus (~100% abundance) has a nuclear spin 7/2, and so a magnetic electron coupled to it can exhibit an absorption spectrum of either 8 symmetric lines (isotropic case), or 8 unsymmetric lines (anisotropic case: 8 parallel and 8 perpendicular features in the first derivative of the spectrum).

For native asphaltenes in general a 16-feature anisotropic spectrum has been observed for this d^1 system in either solid form or in solution in non-polar organic solvents (Fig. 4). Assignment of the absorption lines is in general agreement with the assignment for the axial symmetry case as described previously by O'Reilly[10]. The line positions have been carefully examined in a second derivative format[11], and with multi-amplitude recordings (Fig. 5). The line positions of the vanadium resonance for nine different asphaltenes have recently been measured and are shown in Fig. 6. When compared with a sample of vanadyl etioporphyrin I, whose line positions are also

shown in Fig. 6, a number of additional lines are observed for the asphaltenes. Whether the additional lines represent other paramagnetic species or other structural environments for the vanadium in the asphaltene samples is still unknown. However, such a difference is useful in qualitatively differentiating asphaltenes from different sources.

Another empirical criterion for differentiating among asphaltenes is obtained by measuring the spacings of the $g_{//}$ features: $2_{//} - 1_{//}$ and $8_{//} - 7_{//}$. Tentatively, two parameters can be derived (Table I); one is the $A_{//}$ value which is the average spacing of the parallel features, and the other is the difference of the spacings, Δ, representing a second-order effect arising because of the dependence of the spectrum on the strength of the external magnetic field. The real meaning of the latter quantity has not yet been fully explored, but it is thought to represent deviations from axial symmetry. It appears that all asphaltenes studied here have axial symmetry except for the samples from Bachaquero (CY), Baxterville (GS), and Wafra A-1. Since both the $A_{//}$ and Δ values of Bachaquero (CY) asphaltene differ from those of Wafra A-1 asphaltene, it might be expected that there would be a structural difference between the two asphaltenes. Analysis of the anisotropic spectrum of the asphltenes to yield complete values of $g_{\perp}$, $g_{//}$ and $A_{\perp}$, $A_{//}$ is hindered by overlapping line structures and the difficulty of converting the spectrum into an isotropic one.

Conversion of an anisotropic spectrum ("bound") of the vanadium in asphaltene into an isotropic spectrum ("free") can be effected by dissolving the asphaltenes in a polar solvent such as benzyl n-butyl ether, tetrahydrofuran or diphenylmethane and heating at an elevated temperature[12]. Such a conversion is reversible. From the relative intensities of the isotropic and anisotropic spectra taken at different temperatures, the disassociation energy can be obtained. For a given asphaltene, identical energy values have been observed regardless of the solvent system. The energy values of three asphaltenes are given in Table II. These results suggest that the observed "bound" vanadium is associated with the asphaltene molecule, probably with the aromatic portion. The fact that this "associated" or "bound" type of vanadium becomes disassociated is further supported by dilution studies in a given solvent system. In dilute solutions (~0.4 Wt. %) a nearly isotropic "free" type of spectrum was observed. In solvents with differing basicities the vanadium-containing asphaltene usually shows some indications, though small, of the isotropic vanadium ESR absorptions even at room temperature. The relative effectiveness of solvents for producing the "free" vanadium species may be ranked as follows: diphenylmethane < benzyl n-butylether < 1-ethylnaphthalene < benzene < nitrobenzene < pyridine < tetrahydrofuran.

Nitrogen Superhyperfine Splittings (s.h.f.)

The literature indicates no nitrogen s.h.f. for the oxovanadium (IV) in a quadridentate nitrogen ligand except for the case of vanadyl tetraphenylporphin in chloroform or carbon disulfide "glass" reported by Lee[13]. We have been able to observe nitrogen s.h.f. for vanadyl

phthalocyanine doped at a concentration of 2000 ppm into either a condensation polymer of anthracene or of phenanthrene, or a gilsonite asphaltene (natural vanadium content < 1 ppm). Figure 7 shows the 9-line pattern of nitrogen s.h.f. structures superimposed on the vanadium No. $4_{\perp}$ line for vanadyl phthalocyanine doped into a polymer made from anthracene and formaldehyde. For four equivalent nitrogen nuclei the relative intensities of the nine lines are expected to be 1, 4, 10, 16, 19, 16, 10, 4, 1. The intensity distribution patterns of the nitrogen lines for vanadyl phthalocyanine either in anthracene polymer or in the gilsonite asphaltene drop off rapidly for the outer nitrogen lines, but in general retain the bell shape. However, when 2000 ppm vanadium in the form of vanadyl etioporphyrin I was doped into gilsonite asphaltene or an aromatic medium such as perylene, there were no nitrogen s.h.f. structures observed. On the other hand, there is indication that there may be nitrogen splittings in the petroporphyrins (vanadium) of native asphaltene. The repeated scan of the No. $2_{\perp}$ region in a second derivative format for Bachaquero (VX) asphaltene is given in Fig. 8. In addition to the line shown, fine structure suggestive of nitrogen lines appears in the overlapping region of the Nos. $4_{\perp}$ and $4_{\parallel}$ features. Typical poorly resolved nitrogen lines superimposed on a vanadium line are illustrated in Fig. 9. The coupling constant observed for both the vanadyl phthalocyanine and petroporphyrin (vanadium) is $A_{\perp}^{N} = 2.6$ G. This value agrees with the nitrogen splitting observed for the vanadyl tetraphenylporphin in chloroform or carbon disulfide, $A_{\parallel}^{N} \simeq 2.9$ G., $A_{\perp}^{N} \simeq 2.8$ G.[13]. Roberts, Koski and Caughey[14] attribute the appearance of the nitrogen s.h.f. to a configuration interaction rather than to covalent bonding. At present it seems that the added aromaticity in the macrocycle does possibly bring out the nitrogen s.h.f. It may be that the π-electron system provides excitation for configuration interaction. The slight nitrogen s.h.f. found in asphaltene may indicate that there are minor constituents of the macrocycles in the form of benz-substituted porphins. Such structures have been demonstrated by mass spectrometry to be present in asphaltenes, e.g., the proposed β,β-benzoporphin[15].

Models for Non-porphyrin Vanadium

"Non-porphyrin" is used here to indicate any quadridentate macrocycle which does not belong to the alkyl- or cycloalkano-porphins (Etio and DPEP series), e.g., the rhodoporphyrin[15,16], mixed quaterenes, etc. Two classes of non-porphyrin vanadium were synthesized and characterized by ESR. The first class is vanadyl complexes of the meso-aromatic ring-substituted porphins. This series consists of vanadyl complexes of tetraphenylporphyrin (TPP), tetra-1-naphthylporphin (T1NP), and tetra-4-biphenylporphin (T4BP). The anisotropic scans of the vanadyl derivative of T1NP and T4BP are similar to that of vanadyl TPP. Each of these compounds is a 4 nitrogen ligand system.

The second class is the vanadyl complexes of β-ketoimines, i.e., quadridentate having 2 nitrogen and 2 oxygen donor atoms. This series consists of vanadyl complexes of bisacetylacetone-ethylenediimine (Acen), bisacetylacetonepropylenediimine (Acpn), bisbenzoylacetone-ethylenediimine (Bzen) and bisbenzoylacetonepropylenediimine (Bzpn). The g-values and vanadium nuclear coupling constants for some of the non-porphyrin vanadium model compounds are tabulated in Table III. One of the qualitative features of the vanadium spectra of β-ketoimines is that the Nos. $4_{\perp}$ and $4_{//}$ lines are resolved in contrast to the case of etioporphyrin I.

A plot of A_o vs. g_o (the isotropic coupling constant and g-value respectively) for a variety of vanadyl square-planar complexes, both porphyrin and non-porphyrin, is useful to characterize the particular types of ligands (Fig. 10). Samples at the upper left are those containing ligands which delocalize the unpaired vanadium spins, and these are characterized by low A_o value and a g_o value approaching that of the free electron, $g_e = 2.0023$. Samples at the lower right corner usually have ligands of an electronegative nature, and these are characterized by high A_o values and low g_o values. The average values from the resulting three groups of vanadyl complexes are shown from left to right as: 4 nitrogen type (porphins), 2 nitrogen, 2 oxygen type (β-ketoimines), and the 4 oxygen type (acetylacetonates). It can be predicted that the 3 nitrogen, 1 oxygen type and the 1 nitrogen, 3 oxygen type ligands will also fall into the nearly straight line relationship. The data for asphaltenes (Bachaquero, VX; Boscan, VY) included in the plot were obtained from a polar solution at elevated temperatures. The relative location of these two points falls in the region typical of the 4 nitrogen donor system. It is hoped that by using this plot non-porphyrin types of vanadium chelates contained in asphaltenes may be readily identified.

ACKNOWLEDGMENT

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REFERENCES

(1) T. F. Yen, J. G. Erdman, and A. J. Saraceno, Anal. Chem., 34, 694 (1962).

(2) T. F. Yen, J. G. Erdman, and A. J. Saraceno, Bitumen, Terre, Asphalte, Peche, 15, 141 (1964).

(3) J. Q. Adams, K. H. Altgelt, R. L. LeTourneau, and L. P. Lindeman, ACS, Div. Petroleum Chem., Preprints, 11 (2) B140 (1966).

(4) J. G. Erdman, and J. P. Dickie, ACS, Div. Petroleum Chem., Preprints, 9 (2) B69 (1964).

(5) T. F. Yen, and J. G. Erdman, in "Encyclopedia of X-Rays and Gamma Rays" (G. L. Clark, Ed.), Reinhold Publishing Company, New York, 1963, pp. 65-68.

(6) R. A. Gardner, H. F. Hardman, A. L. Jones, and R. B. Williams, J. Chem. Eng. Data, 4, 155 (1959). In this reference, the term "petrolene" is used rather than resin. These petroleum fractions were thermal diffusion cuts, prepared by Gardner and coworkers from the pentane soluble fraction of an 85 to 100 penetration asphalt derived from a blend of Illinois and Oklahoma crudes by oxidation of a 200 penetration vacuum distillation residuum.

(7) A. J. Saraceno and N. D. Coggeshall, J. Chem. Phys., 34, 260 (1961).

(8) R. A. Friedel, J. Chem. Phys., 31, 280 (1959).

(9) A. J. Saraceno, D. T. Fanale, and N. D. Coggeshall, Anal. Chem., 33, 500 (1961).

(10) D. E. O'Reilly, J. Chem. Phys., 29, 1188 (1958).

(11) C. L. Wolfe, E. C. Tynan, and T. F. Yen, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Paper No. 54, March, 1967.

(12) E. C. Tynan, and T. F. Yen, ACS, Div. Petroleum Chem., Preprints, 12 (2) A89 (1967).

(13) S. K. Lee, M. S. Thesis, UCLA (1964); cf. D. Kivelson and S. K. Lee, J. Chem. Phys., 41, 1896 (1964).

(14) E. M. Roberts, W. S. Koski, and W. S. Caughey, J. Chem. Phys., 34, 591 (1961).

(15) E. W. Baker, T. F. Yen, J. P. Dickie, R. E. Rhodes, and L. F. Clark, J. Am. Chem. Soc., 87, July 5 issue (1967).

(16) M. F. Millson, D. S. Montgomery, and S. R. Brown, Geochim. Cosmochim. Acta, 30, 207 (1966).

(17) L. J. Boucher, E. C. Tynan, and T. F. Yen, to be published.

TABLE I

Empirical Parameters from Anisotropic Spectra

Petroporphyrin Sample	$A_{//}$ (G)	Δ' (G)
Boscan (SR)*, Venezuela	176	4.6
Boscan (VY)*, Venezuela	172	4.0
Baxterville, Mississippi	171	-2.6
Taparito, Venezuela	172	3.6
Bachaquero (CY)**, Venezuela	170	0
Wafra A-1, Neutral Zone	179	12
Wafra 17, Neutral Zone	174	3.1
Bachaquero (VX)**, Venezuela	173	2.1
Mara, Venezuela	172	4.6
VO Etio I (castor oil)	175	11
VO Etio I (in gilsonite)	171	6.7
VO Etio I (toluene)	175	9.3
VO Acac (in gilsonite)	188	0.5
VO Acen (THF)	183	14
VO Bzpn (THF)	179	8.8
VO Bzpn (toluene)	181	8.3

* Boscan (SR) collected in 1959; Boscan (VY) collected in 1962 upper and lower Boscan sand.

** Bachaquero (CY), Maracaibo; Bachaquero (VX), Well Largo.

TABLE II

Activation Energy of Association for Vanadium in Asphaltenes

Asphaltene	V Content (ppm)	Dissociation Energy (kcal)
Bachaquero (VX)	2700	14.3
Boscan (VY)	4700	10.0
Gilsonite (CB) doped*	2700	10.4

* with vanadyl etioporphyrin I.

TABLE III

Vanadium Nuclear Hyperfine Splittings and g-Values for Non-porphyrin Model Compounds

Vanadyl Complex*	A_o**	g_o	$A_{//}$**	$A_{\perp}$**	$g_{//}$	$g_{\perp}$
Acen	101.7	1.974	182.5	61.3	1.957	1.982
Acpn	102.5	1.974	183.8	60.4	1.945	1.999
Bzen	102.4	1.975	183.3	62.0	1.952	1.986
Bzpn	103.4	1.975	182.5	63.9	1.953	1.986

* in THF.

** in Gauss.

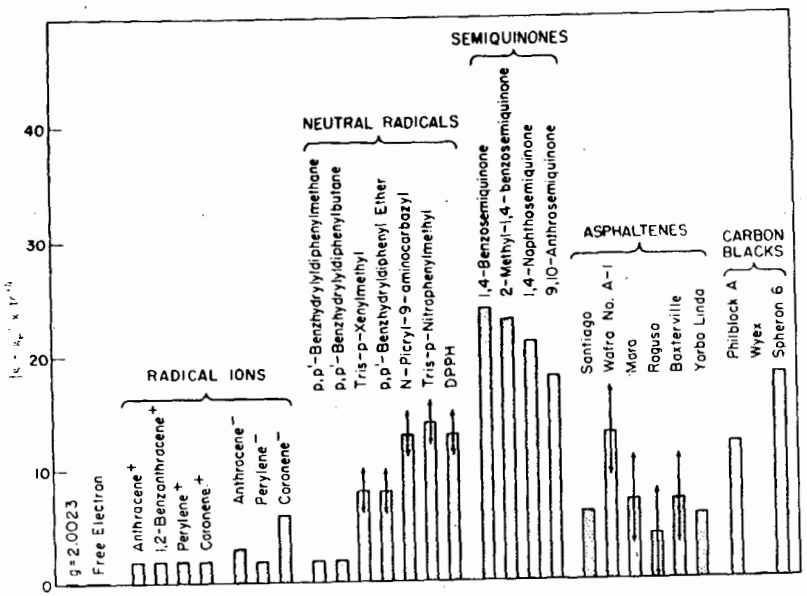


FIGURE 1: Lindé g-Values of Petroleum Asphaltenes and Other Radical-Containing Substances.

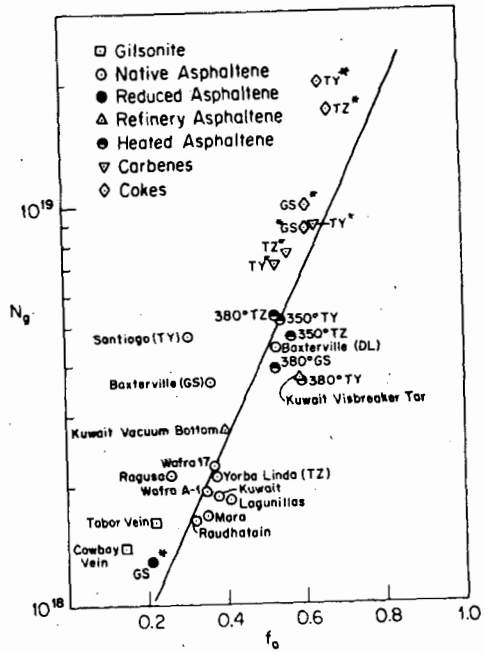


FIGURE 2: Dependence of Spin Concentration on Aromaticity.

(* A fraction from the corresponding asphaltene.)

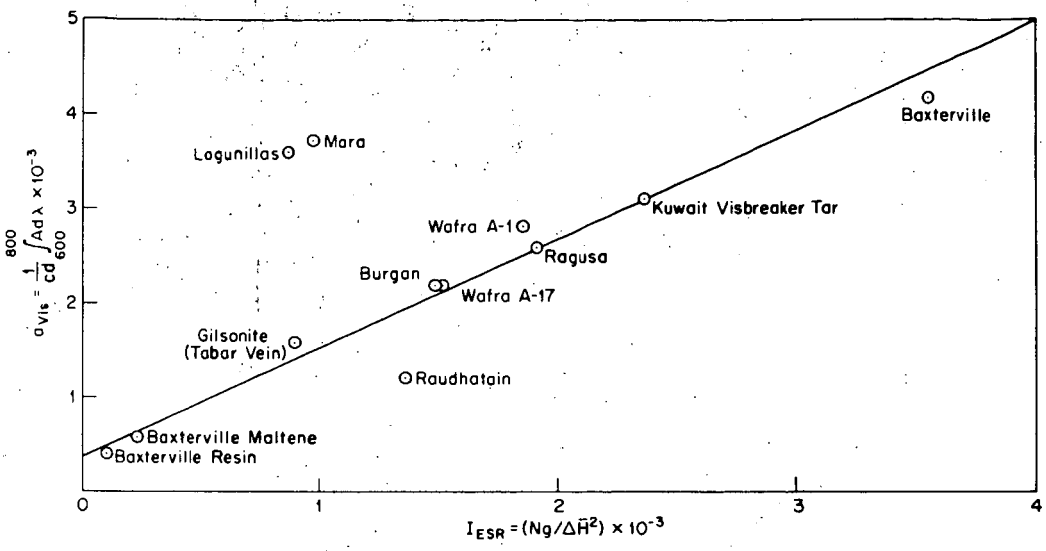


FIGURE 3: Integrated Visible Spectral Absorptivity vs. ESR Free Radical Absorption Intensity.

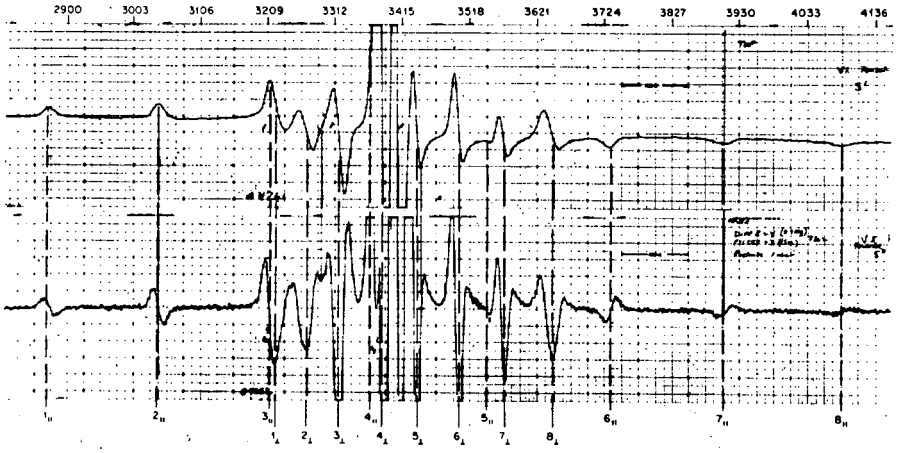


FIGURE 4: Vanadium Anisotropic Spectra of a Bachaquero (VX) Asphaltene (Upper, First Derivative Format; Lower, Second Derivative Format).

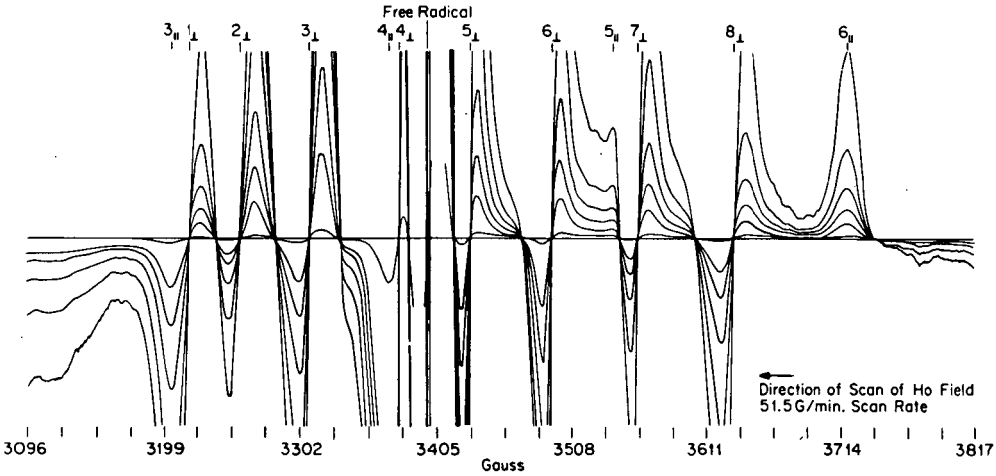


FIGURE 5: Central Portion of an Anisotropic Vanadium Spectrum from a Multi-amplitude Recording

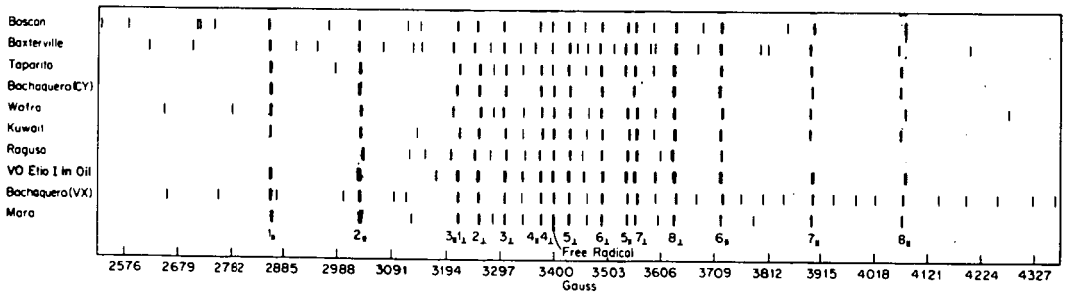


FIGURE 6: Field Positions of ESR Spectra of Native Asphaltenes

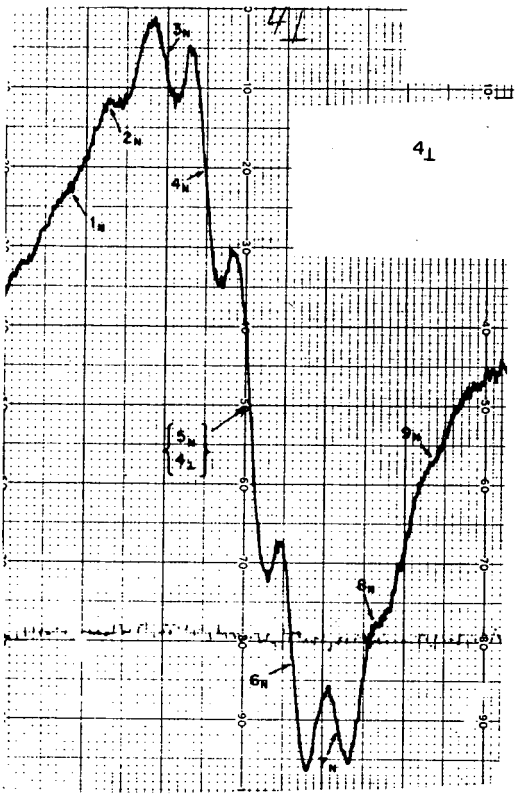


FIGURE 7: Nitrogen s.h.f. Structures of Vanadyl Phthalocyanine-Doped Anthracene Polymer

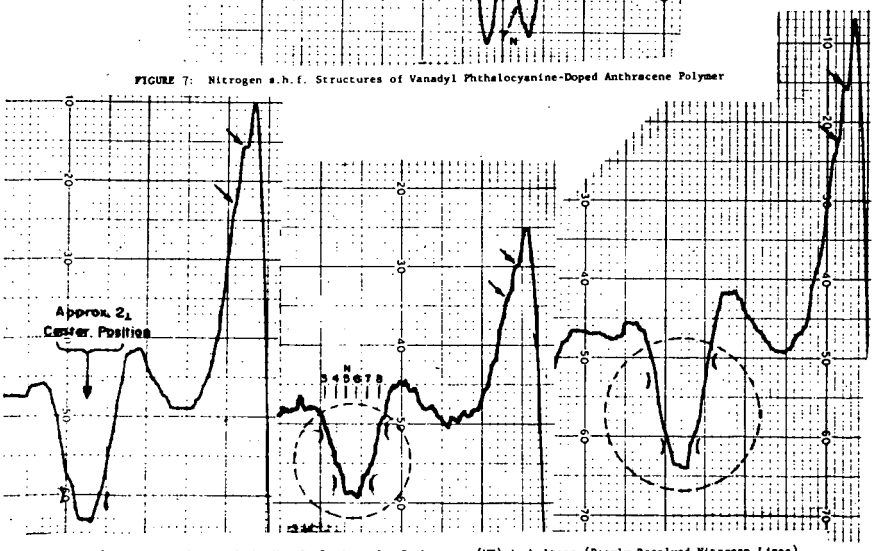
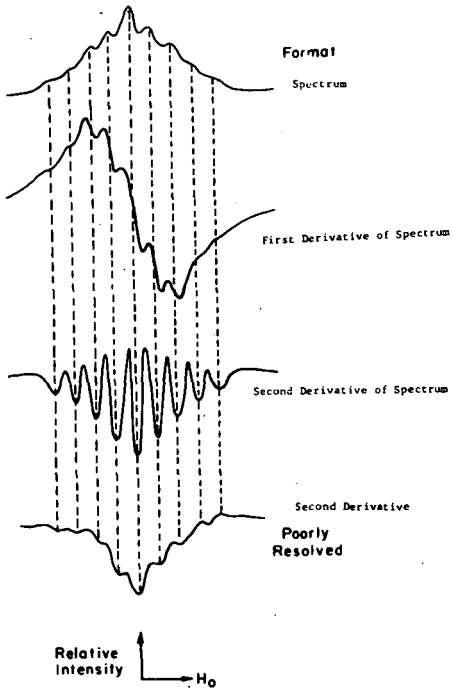


FIGURE 8: Repeated Scans of the No. $2_\perp$ Region of a Bachaquero (VX) Asphaltene (Poorly Resolved Nitrogen Lines).

FIGURE 3: Nitrogen s.h.f. Lines Superimposed on Vanadium Lines (Typical Case).



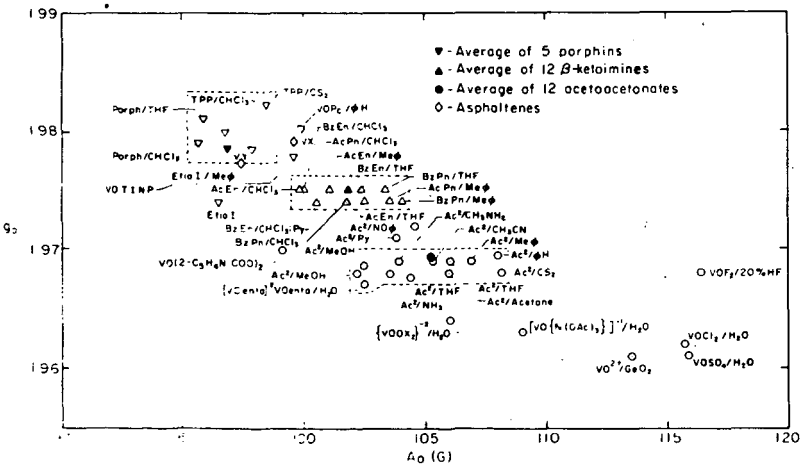


FIGURE 1 : Relationship Between g_0 and A_0 for a Series of Vanadyl Ligands