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ESR STUDY OF VANADYL CHELATES IN CARBONACEOUS MESOPHASE

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Behavior and arrangement of Gachsaran residue in the magnetic field during the carbonization process were investigated through the ESR spectra from spin-probes of the vanadyl porphyrin chelates. The results show that some of the chelates are incorporated into formed mesophase and that the molecular plane is oriented parallel to the field.

Optically anisotropic mesophase spherules are now well-known to develop and grow on the carbonization process of pitches, reduced crudes, coals, and some kinds of organic compounds.[2,3] Sanada et al.,[4] Singer and Lewis,[5] and Imamura et al.[6] investigated orientation of the mesophase in the magnetic field by means of the polarized-light microscopy. Recently, it has been reported that some metals in the petroleum residues are concentrated in the mesophase.[7] In connection with these works, we attempted to obtain information from a different point of view on the growth of the mesophase and on the behavior in the magnetic field on the basis of the ESR spectra of vanadyl porphyrin chelates naturally existing in the petroleum heavy oils as paramagnetic probes.

Gachsaran residue (IH) containing the vanadyl chelates (306 ppm as vanadium metal) was used in the present study. In order to heat the sample in the magnetic field and to measure the ESR spectra in situ, a new apparatus available for observation of spectral change at high temperatures to ca. 500°C was constructed for these experiments the temperature could be attained by hot air passing through a spiral silicon-carbide heater installed just under the cavity. ESR spectra were recorded on an X-band spectrometer (JEOL JES-ME-3X). The sample was heat-treated in a helium atmosphere of 300 mmHg or in a flow of nitrogen gas.

Temperature Dependence. When the original IH sample was heated to 430°C in helium gas, remarkable spectral changes were observed near ca. 300 and 430°C. The typical spectra are represented in Figs. 1 (a)-(c). The anisotropic structure at room temperature is very similar to that previously reported[8,9] and the parameters, g and A, calculated from the spectrum are comparable to those of pure vanadyl porphyrin complexes.[10] Therefore, the spectrum is considered to be due to vanadyl chelate complexes coordinating to porphyrin rings. But no further information on the structure can be derived from this spectrum, because it consists of many components from the mixture of porphyr substituents.[11] A spectral line at g=2.002, which is superimposed with the signals identified to the porphyrin chelates is assigned to free radicals always contained in asphaltenes. With the rise of temperature, the value of coupling constant for the parallel component became gradually smaller and that of the perpendicular component larger. The conversion of the anisotropic spectrum into the isotropic one appeared at the elevated temperature near 300°C. However, an anisotropic structure emerged again in the vicinity of 430°C. Appearance of the anisotropy by heating was found to be irreversible. Reappearance of the anisotropy suggests that some change in the structure was induced by such heating of the sample and that the molecular motion was so hindered in the changed structure as not to produce sufficient averaging of anisotropy. Taking into account the formation of mesophase at the same temperature,[12)] the change in the structure detected by ESR is directly related to the mesophase spherules in the sample.

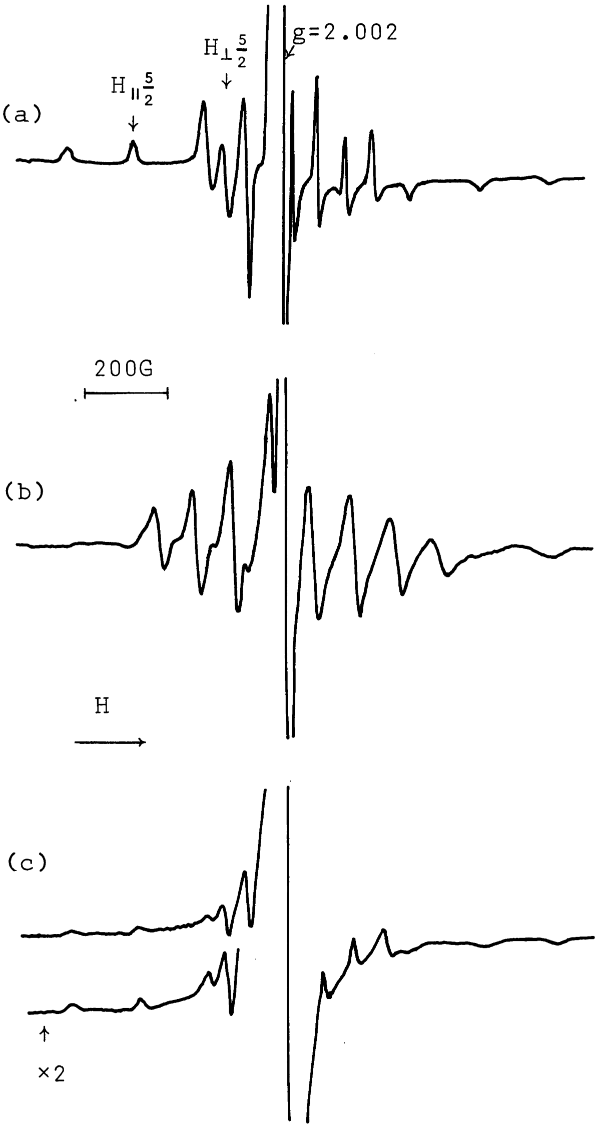

Fig. 1. ESR spectra of IH at (a) room temperature, (b) 390, and (c) 430°C.

Magnetic Field Dependence. The IH sample was treated at 450°C for 30 min in the various magnetic fields and then cooled to room temperature. It is reasonably assumed that the orientation of the mesophase caused by the magnetic field was frozen at room temperature by this procedure. Thus, one can obtain the information on the orientation by magnetic field at such higher temperature like 450°C. The intensity ratio of the parallel to perpendicular part at the I=5/2 component of the spectrum was plotted against the field strength (Fig. 2). According to the method by Schwerdtfeger and Diehl,[13)] the degree of order, s, defined by the following equation was estimated to be -0.09 in the field of 10 kgauss, using the same distribution function as Meier and Saupe[14)] introduced.

$$s = \langle 3\cos^2\theta - 1\rangle/2$$

where θ is the angle between the symmetry axis and the optic axis of the liquid crystal. The value is considerably small, compared with that of pure liquid crystals. The chelates out of the mesophase might contribute to reduce the degree of order, as well as disturbance due to bubbling of decomposed gas and so on.

Angular Dependence. The sample in the cavity was heat-treated in the field of 10

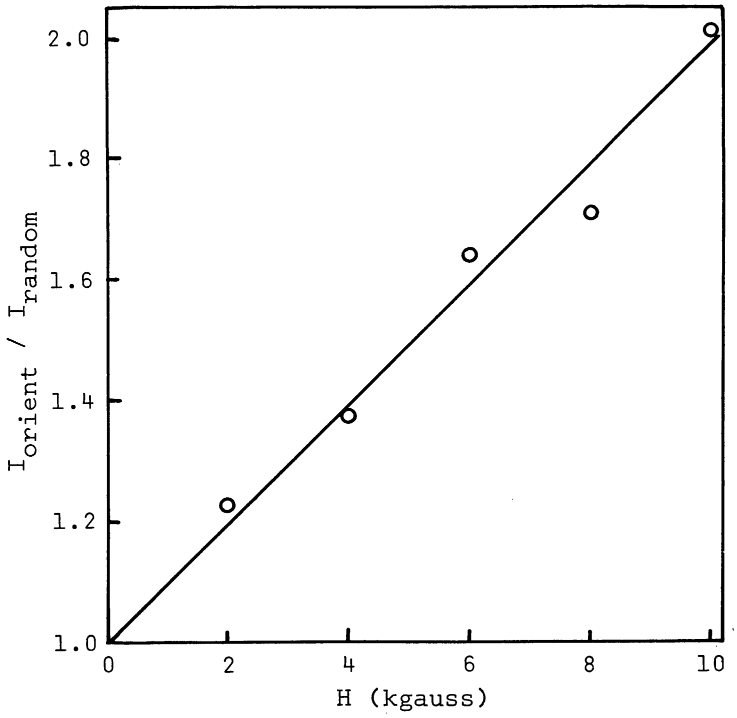

Fig. 2. The relation between field strength (H) and intensity ratio of oriented spectrum to random one (I_{orient} / I_{random}).

kgauss at both 350 and 450°C and then cooled to room temperature. The spectra were measured in situ by rotating the sample tube around the axis perpendicular to the magnetic field. As can be seen from Fig. 3, the spectrum is little affected by the rotation for the sample heat-treated at 350°C, whereas the ratio of $I_{\parallel 5/2}$ / $I_{\perp 5/2}$ changes from 0.166 to 0.476 when treated at 450°C. The high value of $I_{\perp 5/2}$ at 0° implies that the number of molecules whose axis is perpendicular to the field is larger than that parallel to the field. From the fact that the layers in the mesophase composed of planar aromatic molecules align parallel to the applied field,[5,6] it is evident that the vanadyl chelates are interposed between the layers and behave together with the mesophase in the magnetic field. In addition the increase of $I_{\parallel 5/2}$ with the rotation can be explained in the following way: since the c-axis of the mesophase is allowed to take any directions in the plane perpendicular to the field, the chelates in the mesophase whose c-axis is vertical to both the field and the sample tube make positive contribution to the intensity of the parallel component, for example $I_{\parallel 5/2}$, with the rotation of the sample tube.

In conclusion, it was found that some of the vanadyl porphyrin chelates in Gachsaran residue are involved along the lamellae in the mesophase developed at 430°C and behave in the same manner as the mesophase toward the applied field.

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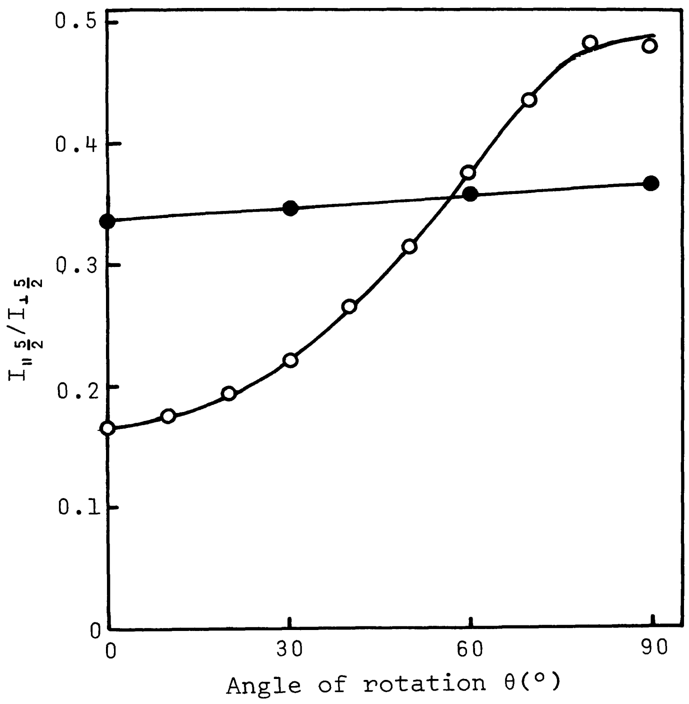

Fig. 3. The angular dependence of the intensity ratio, $I_{\parallel 5/2} / I_{\perp 5/2}$ for IH heat-treated in the field of 10 kgauss.

● : heat-treated at 350°C for 30 min.

○ : heat-treated at 450°C for 30 min.

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