

# STUDY OF CARBONACEOUS MESOPHASE THROUGH THE ESR SPECTRA OF VANADYL CHELATES

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## Introduction

Orientation of optically anisotropic mesophase spheres in the magnetic field has been investigated by means of the polarized-light microscopy [1-3]. Our study was initiated to draw information from a different point of view on the mesophase conversion and on the behaviors in the magnetic field on the basis of the ESR spectra of paramagnetic vanadyl chelates in the mesophase. Also, from the spectra observed at elevated temperatures rotational correlation times of the chelates were estimated as a kind of the fluidity during the carbonization process and the activation energy obtained from the temperature dependence of the correlation times was discussed in relation to the size of the mesophase.

## Experimental

Iranian heavy oil (IH) was used as one of petroleum heavy oils with high vanadium content (306 ppm as vanadium metal). On the other hand, vanadyl tetraphenylporphyrin which is similar to vanadyl chelates existing in the heavy oils, was doped to Ethylene tar pitch (ET) free from vanadium.

In order to heat the sample in the magnetic field and to measure the ESR spectra in situ the samples were heat-treated in nitrogen atmosphere in the cavity, which had been specially designed for this experiment. By this cavity it was possible to make such a heat-treatment and observation of spectral changes at higher temperatures to about 500°C: for a temperature variation experiment, temperature of a sample in the cavity was controlled by hot air passing through a spiral silicon-carbide heater installed just under the cavity.

## Results and Discussion

When the original IH sample was heated to 430°C, 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 similar to that previously reported and the ESR parameters are comparable to those of pure vanadyl porphyrin complexes [4]. Therefore, the spectrum is considered to be due to vanadyl chelate complexes coordinating to porphyrin rings.

The conversion of the anisotropic spectrum into the isotropic one appeared at the 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: once the anisotropic pattern was formed, no isotropic spectrum was observed in the range between 430°C and room temperature. It suggests that some change in the structure was induced by such heating of the sample and that the molecular motion was so hindered on the changed structure as not to produce sufficient averaging of anisotropy.

The spectral changes similar to those of IH were observed also in the case of ET doped vanadyl tetra-

phenylporphyrin. However, the spectrum gave only isotropic structure in the range of about 250-400°C. The anisotropic spectrum occurred with the treatment at 400°C for 2 hr.

The IH sample was treated at 450°C for 30 min in the various magnetic fields and then frozen to room temperature. Thus, one can obtain information on the orientation by magnetic field at such higher temperature like 450°C, since the vanadyl chelates are reasonably assumed to be involved into the formed mesophase [5] and to behave in the same manner to the mesophase. According to Schwerdtfeger and Diehl [6], the intensity ratio is related to an ordering parameter,  $s$ , which is a measure of the arrangement of the mesophase:

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

where  $\theta$  is the angle between the symmetry axis and the optical axis of the liquid crystal. It is apparent that the ordering parameter increases linearly with the magnetic field (Fig. 2), but the value at 10 Kgauss, -0.09, is considerably small, compared with that of pure liquid crystals.

The IH sample in the cavity was heated in the field of 10 Kgauss at 350 and 450°C for 30 min and then cooled to room temperature. The spectra were recorded in situ by rotating the sample tube from 0 to 90° around the axis perpendicular to the magnetic field. As can be seen in Fig. 3, the sample treated at 450°C represents the large angular dependence, while the spectrum is little affected by the rotation for the sample heat-treated at 350°C. On the other hand, the intensity ratio of the parallel part to the perpendicular one for ET treated at 400°C for 2 hr also changes with the rotation, although the angular dependence is smaller than that of IH treated at 430°C for 30 min. The mesophase has a stacking texture of the lamellae which consist of large aromatic molecules. Accordingly, when the magnetic field is applied, c-axis of the mesophase is considered to be aligned perpendicular to the field because of diamagnetism due to aromatic sheets. If the chelates are incorporated between and/or in the lamellae, one can explain reasonably the high value of perpendicular component at 0°. In addition, the increase of  $I_{\parallel}/I_{\perp}$  with the rotation can be interpreted as follows: 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, for example  $I_{\parallel}/I_{\perp}$  with the rotation of the sample tube.

In liquid, in which Brownian motion is sufficiently rapid, the anisotropy of the ESR spectrum is averaged out and appears isotropic. For this case the Kivelson's theory [7] is the most convenient for the analysis of the experimental results. The correlation time  $\tau_c$  is estimated by using the theory from the line widths and the heights at each temperature at which the isotropic spectrum appears. Fig. 4 shows the changes of  $\tau_c$  with the reduced temperature. The correlation time of each sample decreased with rising temperature, but it increased drastically

near 370-390°C. From the fact that no sphere is observed micrographically at these temperatures, one can say that the mesophase precursors presumably begin to grow in the matrix.

The activation energy was estimated to 15.8 Kcal/mol for IH and 4.8 Kcal/mol for ET from the slope of straight line at the range of lower temperature. The optical micrograph of IH treated at 430°C for 30 min shows the very small spheres of 1-5  $\mu$ m, while the large size of mesophase appeared in the matrix of ET treated at 400°C for 2 hr. The relation between the sizes of the mesophase spheres and the activation energy of the vanadyl chelates in IH and ET suggests that the high activation energy accompanied by the drastic appearance of the mesophase results in the formation of the small spherulites.

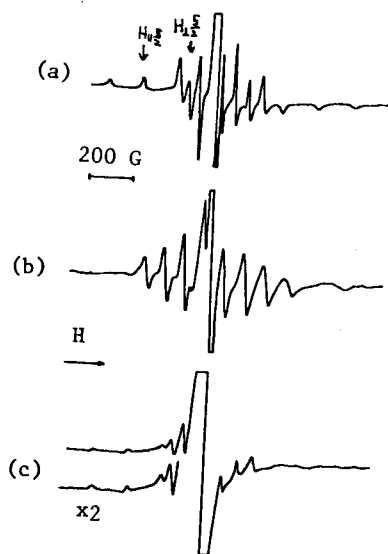


Fig. 1 ESR spectra of IH at (a) room temperature, (b) 360 and (c) 430°C.

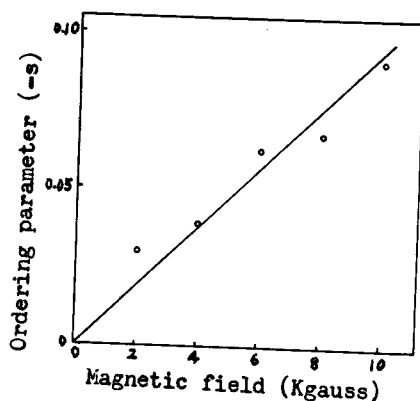


Fig. 2 Variation of ordering parameter for IH with the magnetic field.

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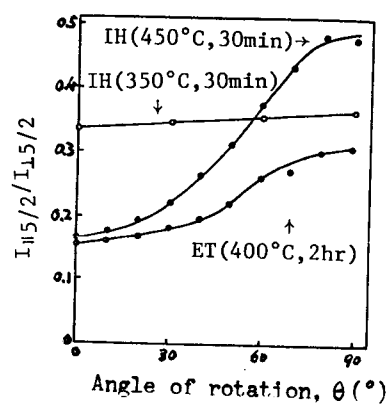


Fig. 3 Angular dependence of the intensity ratio,  $I_{1/2}/I_{1/2}^F$ , for IH and ET heat-treated in the field of 10 Kgauss.

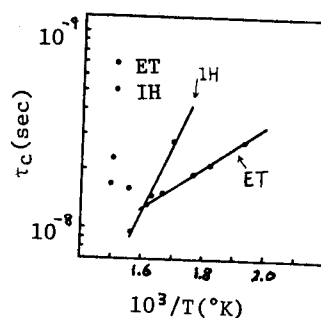


Fig. 4 Variation of correlation time for IH and ET with temperature.