Electron Spin Resonance and Colloidal Properties of Crude Oil

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RECENT EXPERIMENTS have shown that crude oils are colloidal systems (9) and that many crude oils exhibit electron resonance (12). Also, it has been reported (4) that the material giving rise to the electron paramagnetism in a sample of Mississippian crude oil from the Illinois Basin could be concentrated by ultracentrifugation in the sediment and bottom liquid fractions. It was concluded that the paramagnetism in this crude oil is associated with asphaltene materials and is closely related to the electron paramagnetism exhibited by coals, amorphous carbons, and similar substances (1, 6, 8, 10).

In this study, the relationship between the colloidal properties and electron paramagnetism of crude oils has been investigated further. An attempt has been made to suggest further applications of electron paramagnetic resonance to the understanding of these systems.

EXPERIMENTAL PROCEDURE AND RESULTS

Four crude oils of different geological ages from the Illinois Basin were diluted with *n*-heptane in a 1 to 1 volume ratio and centrifuged at approximately 80,000 times gravity in a Spinco Model L ultracentrifuge. The amount of sediment was measured at various times during the centrifugation and in all cases reached its limiting value, within experimental error, in less than 290 hours. Figure 1 shows the amount of sediment obtained for each of the crude oils as a function of time.

The amounts of sediment from these four crude oils were then compared with the relative intensities of the electron spin resonance of the crude oils. The spectrometer is a conventional X-band microwave bridge system (4). The relative intensities of the absorption lines were determined by comparing the peak amplitudes of the derivative curves corrected for the differences in the line width of the samples. This procedure assumes that the absorption curves have the same line shape. In all of the samples reported here, the absorption line was single and only a few gauss wide, with no evidence of any hyperfine structure. A comparison of the line widths, electron spin resonance (ESR) absorption intensities, and amounts of sediment for these oils is given in Table I. Also shown in Table I are the relative optical absorption coefficients at 500mμ for solutions of these crude oils in *n*-heptane at dilutions from 50:1 to 400:1. In the centrifugation experiments, the supernatant liquid was essentially colorless; the color of the crude oil was due to the colloidal particles.

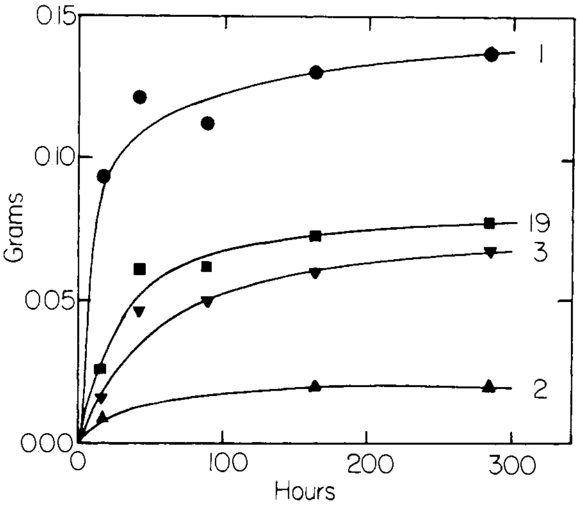

Figure 1. The amount of sediment obtained from several crude oils as a function of time. The ultracentrifuge was operated to give about 80,000 G

Table I. Summary of Sedimentation, Optical, and Electron Spin Resonance Measurements of Crude Oils

	Sample	δH[a] Gauss	ESR Abs.[b] (Crude Oil)	500 Mμ Abs.[b]	Sediment[b] (283 Hr.)	Wt. % Sediment
1	(Mississippian)	5.00	1.00	1.00	1.00	3.6
19		5.20	0.50	0.54	0.58	2.1
3	(Pennsylvanian)	5.45	0.48	0.47	0.50	1.8
2	(Devonian)	[c]	0.18[c]	0.19	0.15	0.6

[a] Line width, δH, is the separation between the maximum and minimum of the first derivation of the absorption.

[b] Relative values referred to sample 1.

[c] The ESR absorption line for this sample was too weak to obtain a value for δH; therefore, the ESR intensity is uncorrected for changes in δH.

Straight lines are obtained if the values in Table I for the optical and ESR absorption are plotted against the amount of sediment in the crude oils. A larger group of crude oil samples from the Illinois Basin, though not centrifuged to equilibrium, also showed approximately the same linear relationship between the sediment and the ESR intensity. The apparent optical absorption includes the effects of scattering which, however, will not be great because of the small size of the particles (9).

Further ESR observations were made on two of the Mississippian crude oils. The line width and the G-factor were measured for the crude oils, sediments and bottom liquid fractions. For all samples whose G-factor was measured the value of 2.0034 ± 0.0004 was found. Table II gives the values obtained for the line widths. The electron spin resonance of a crude oil, sample 2, which showed a weak resonance was also examined to determine the effects of evacuation and of heating. The electron spin resonance of other carbon samples varies greatly for different tem-

Table II. Electron Spin Resonance Line Widths for Various Crude Oils and Fractions

Sample	δH
Oil 1 (Mississippian)	5.00 ± 0.10 gauss
Bottom liquid fraction	5.75
Oil 16 (Mississippian)	4.25
Bottom liquid fraction	6.35
Resuspended sediment	4.65
Char from oil 2[a] (Devonian)	3.35

[a] Sample evacuated and heated to 350° C.

peratures of heat treatment and pressures of oxygen (*1, 5, 6, 8, 10, 11*). However, no change in the electron spin resonance of the oil sample was found upon evacuation. Moreover, heating in vacuum to a temperature of 200° C. had no effect. Upon further heating to approximately 350° C., the oil sample formed a char which showed a very strong resonance. The line width of this char is also included in Table II.

Although conditions for the most part were held constant in the experiments, results were occasionally obtained which were not reproducible. These may have been due to aging processes or to slow interactions with atmospheric oxygen, but at present the details are not clear.

DISCUSSION OF RESULTS

The direct proportionality of both the optical and ESR absorption to the amount of sedimentable material in many crude oils of different origin contrasts with the sensitivity to temperature and atmosphere of the ESR absorption in carbon and charcoal. This result suggests that the geological conditions governing the amount of sediment in these oil samples were relatively constant, differing in degree but not in general nature, As to the relation between optical and ESR absorption, Friedel (*3*) has suggested the part of the ultraviolet absorption of coals might be a result of free radicals which are known to be present (*1, 5, 10, 11*). The proportionality of the ESR and optical absorption to the amount of sediment material suggests that absorption measurements, if properly calibrated, can be used for routine determination of the colloidal material in oil, instead of the more time-consuming sedimentation method.

The ESR line widths in Tables I and II reveal that measurable differences exist between the various samples. Effects governing δH for carbon samples have been considered (*2*). The most important factors are probably exchange narrowing and the amount of spatial delocalization of the unpaired electron. The latter effect is important in aromatic hydrocarbon negative ions (*7*), where increased delocalization of the unpaired electron reduces the hyperfine splitting and broadening of the ESR absorption by the protons. Other effects such as line broadening due to anisotropic G-factors and anistropic diamagnetic susceptibilities (*2*) probably contribute, but to a lesser extent.

Most of the differences in δH for the samples reported here can be explained in terms of the dependence of line width upon the "size of the free radical." Thus, one would expect δH for liquid fractions remaining after centrifugation to be larger than for the original oil. The unpaired electrons in such fractions must be contained in particles smaller than average; they would, therefore, have a higher probability of being associated with smaller aromatic ring systems. On the other hand, one would expect the line width in the oil char, produced by the carbonization process at 350° C., to be narrower than in the crude oil because the particles and presumably the odd-electron ring systems are larger. These expectations are borne out by the data given in Table II. The line widths in the bottom liquid fractions average 1.5 gauss broader than the 5-gauss width found in the original oils, while the line width of the char is the narrowest. However, the line width found for the resuspended sediment is slightly greater than that in the oil, whereas one would expect it to be smaller because the particles should be larger. Of course, the sedimentation and resuspension in a different medium could modify the carbonaceous free radicals.

The data given in Table I suggest that there may be an interesting inverse correlation between the ESR line width and the amount of sediment in the crude oils. The line width increases from 5.00 to 5.45 gauss while the weight per cent of sediment decreases from 3.6 to 1.8. This implies a larger average particle size for the oil having the greater amount of sediment, which is reasonable. Support of this interpretation is afforded by the approximate molecular weights and amounts of the sediments (Mississippian > Pennsylvanian > Devonian) determined for these same oils in the earlier ultracentrifuge experiments (*9*).

Such a correlation between particle size and amount of sediment could arise in several ways, depending upon the mechanism responsible for the formation of the colloidal particles. In fact, more detailed studies could lead to a better understanding of the geological conditions under which the crude oil iself was formed. As for the particles, in a thermal process one would expect the amount of "cracking" and the particle size to increase with temperature and with the length of time the oil was heated. However, it seems unlikely that the two variables would affect the particle size distribution in the same manner. Another explanation of the correlation between particle size and per cent sediment is that most of the solid particles have been filtered out by the passage of the oil or its precursor through rock strata in the course of its geological history; the more porous the rock, the larger the amount of sedimentable material remaining and the larger the average particle size.

This study, intended mainly as an exploratory venture, suggests further work of this nature is worthwhile. For example, the geological implications should be investigated. One approach would be to attempt to reproduce the colloidal and ESR characteristics of a crude oil by thermal treatment of the supernatant liquid from a centrifuged sample. It would be interesting to fractionate the particles according to size by careful centrifugation and obtain a quantitative comparison of the ESR absorption with particle size. Moreover, in the case of carbon samples, it has been found (*5, 11*) that the concentration of unpaired electrons as well as the ESR line widths depend upon the carbon-hydrogen ratio, and similar studies might be made of the sediment.

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