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SHALE OIL CHARACTERIZATION BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND OPTICAL ACTIVITY DETECTION

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SUMMARY

Chromatograms are obtained for various saturated fractions of shale oil, having different particle sizes and from different sources. Separation is accomplished by reversed-phase high-performance liquid chromatography and the eluate is monitored by an optical activity detector. The chromatograms show an abundance of optically active components, which may be good fingerprints for the various shale oils.

INTRODUCTION

The proper characterization of any fossil fuel is important to its utilization and to exploration efforts for its reserves. Shale oil is particularly interesting because its reserves are known to be substantially larger than petroleum reserves[1]. Of the many physical and chemical properties suitable for characterization of shale oil, perhaps the most interesting is the associated optical activity. Optical activity is generally considered to be evidence for biological activity, past or present. Unlike the more reactive functional groups in the molecule, the chiral centers may be retained despite the hostile conditions that led to the formation of fossil fuels. Optically active materials have been found in the montan wax of brown coal[2], oil distillates from coal[3], petroleum distillates[4], lubricating oils[5], and shale oil[6]. The observed bulk optical rotation has been correlated with retorting conditions[6], geological source[5], aromatic/aliphatic ratio[4], geological age[4], distillate fraction[7], and thermal history[6]. Because of the relatively small amounts of optically active materials that are present, typically very small rotations are observed. And, because of the highly colored nature of most of these materials, measurements are sometimes impossible to obtain.

It is appropriate to ask the question how significant the bulk optical activity is in any correlation scheme. The reason for this is that optical rotation can be dextrorotatory or levorotatory, and both types have been found in fossil fuels[3]. The presence of materials of both classes will cause a cancellation in the observed quantity. The bulk optical rotation is then only an indication of the minimum amount of chiral materials in the sample. It is, therefore, highly desirable to perform some separation on the sample before the measurement of optical activity. Separation also

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allows one to determine the individual contributions of the various components to further refine any correlations.

The technique of choice is then liquid chromatography (LC) in conjunction with optical activity detection[8]. This new technique has been made possible because of the greatly increased sensitivity offered by laser optics over conventional spectropolarimeters. In applications to studies of carbohydrates in urine[9] and of cholesterol and cholesteryl esters in serum[10], detectabilities are in the order of 100 ng of injected amount. In terms of actual rotations, this corresponds to angles of the order of 10^{-5} degrees. We can estimate the applicability to shale oil characterization since a bulk value of $[\alpha]_D^{25} = 0.8°$ is typical of these samples[6]. To avoid overloading, at most 10 mg of sample can be injected using a standard high-performance liquid chromatographic (HPLC) column. And, assuming that twenty different chromatographic peaks contribute to the total signal, one can expect the order of 1/2000 of the bulk specific rotation, *i.e.*, $4 \cdot 10^{-4°}$, to be observed for a peak elution volume of 1 ml. This then is within the useful range of the technique.

EXPERIMENTAL

Materials

Various shale oil samples were obtained from the Laramie Energy Research Center, U.S. Department of Energy (Laramie, WY, U.S.A.). To obtain the saturates, a 0.5-g sample of dried oil was dissolved in 20 ml of cyclohexane. The solution was cooled to 0°C in a circulating cold bath, and 10 ml of 15% phosphorous pentoxide in sulfuric acid was slowly added with stirring. Stirring was continued for 1 h. The mixture was then transferred and centrifuged for 30 min at 11,000 *g*. The cyclohexane layer was drawn off, and the bottom layer was twice more mixed with 10 ml of cyclohexane and centrifuged. The combined solution was then evaporated under nitrogen and weighed. An appropriate amount of acetonitrile was then used to redissolve the residue under ultrasonic agitation to be used for chromatography. All reagents used were reagent-grade material without further purification.

Chromatography

Separation was performed on a 25 cm × 4.6 mm I.D., 10-μm C_{18} column (Alltech, Deerfield, IL, U.S.A.). Samples were eluted with pure acetonitrile as the mobile phase at a flow-rate of 0.8 ml/min. All injections were made through a 200-μl sample loop at a conventional injection valve (Rheodyne, Berkeley, CA, U.S.A.; Model 7010). To reduce any pressure fluctuations caused by the pump (Milton Roy, Riviera Beach, FL, U.S.A.; Model 196-0066-001) at the detector, we used a commercial pulse dampener (Handy and Harman, Norristown, PA, U.S.A.; Model Li-Chroma-Damp II).

Optical activity detection

The basic arrangement for an optical activity detector for LC has been reported earlier[8,9]. In this work, 20 mW of 514-nm radiation from an argon ion laser was used. The flow cell was 10 cm long, with an internal volume of 200 μl. To eliminate the need to provide large currents for modulation in the air-based Faraday rotators, we instead used the eluent in the flow cell as the medium for polarization modulation.

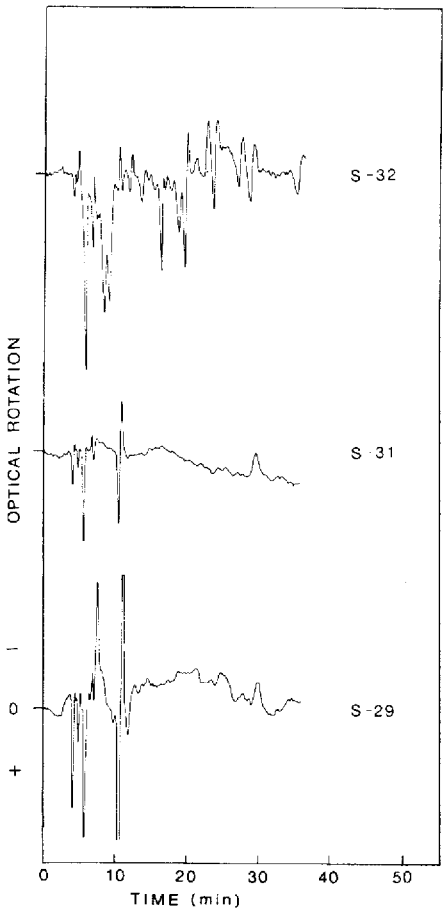
The higher number density of molecules in the liquid *versus* in the air effectively provides a much larger Faraday effect. Since this is done without introducing additional optical components in the cavity, the favorable extinction ratio is preserved. One can then reduce the current by a factor of 1000, or reduce the number of turns in the solenoid correspondingly. In either case, the electrical power requirement is much lower, thus shortening the warm-up period. The decrease in inductance in the solenoid also allows higher frequencies to be used in the modulation if desired. It is true that fractional fluctuations in the number and type of molecules in the region of the magnetic field will cause fluctuations in the modulation. However, these are expected to be negligible in our experiments. Application to gradient elution will be difficult, but not impossible, and the air-based Faraday rotators[8] will have to be used instead.

To accomplish the above, we machined the outer core of the flow cell to 1.3 cm O.D. and wound 420 turns of No. 22 magnet wire in each of two 2.5-cm long regions. The two are driven in opposing field directions at alternate half-cycles of the modulation by switching transistors. A 10-Ω resistor is put in series with the coils to allow the use of a moderate voltage in the modulation, since the solenoids have internal resistances of only 1.2 Ω. Using an independent air-based Faraday rotator as before[8] to provide a standard optical rotation, we have determined that the detectability of the system is $1.5 \cdot 10^{-5}$° (signal-to-noise ratio = 3) for a time constant of 10 sec. For the studies here, a time constant of 3 sec was found to be adequate and was used throughout.

RESULTS AND DISCUSSION

The chromatograms that are obtained naturally depend heavily on the mode of extraction of the material injected. The particular procedure here is chosen to favor the saturated hydrocarbons, which are known contributors to observed optical activity in fossil fuels. So, although nearly all of the optically active components are found in this fraction in petroleum[11], the situation may be different in shale oil. Also, acetonitrile was chosen as the solvent and the eluent to eliminate the solvent front associated with the injection process. This way, events very early on in the chromatogram can be recorded faithfully. There is, however, no guarantee that all interesting components will be eluted during a run of 40 min, or that this choice of eluent/stationary phase is the best. Still, within these guidelines, the studies here provided some interesting results.

Two different groups of chromatograms are shown in Figs. 1 and 2. In Fig. 1, the saturates are derived from Anvil Points shale having various particle sizes. Going from bottom to top, the particle sizes are 0–2.5 cm (S-29), 2.5–7.5 cm (S-31), and 7.5–15 cm (S-32). In Fig. 2, the saturates all have similar particle sizes (0–2.5 cm) but have different origins and qualities. Going from bottom to top, they represent Utah Shale of 12 gallons/ton (S-34), Anvil Points Shale of 25 gallons/ton (S-29), and Colony Shale of 35 gallons/ton (S-38). To compare these chromatograms properly, one needs to recognize that the vertical scales are somewhat different for each one. Variations in the laser power, optical alignment, electronic gain, and modulation conditions can alter the vertical scale. Fortunately, these can be calibrated using a d.c. solenoid to produce a known degree of polarization rotation. These instrumental factors result in scale expansions of 1:0.93:0.67 for S-29:S-31:S-32 in Fig. 1, and 0.87:1:0.87 for S-



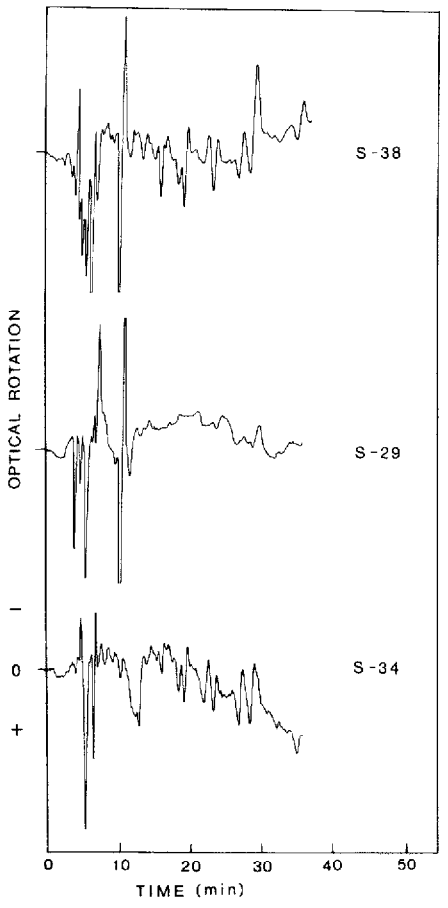


Fig. 1. Chromatograms of shale oil extracts for various particle sizes: S-29, 0–2.5 cm; S-31, 2.5–7.5 cm; S-32, 7.5–15 cm. For vertical scale see text.

Fig. 2. Chromatograms of shale oil extracts for 0–2.5 cm particle sizes and different origins. S-34, Utah Shale (12 gallons/ton); S-29, Anvil Points Shale (25 gallons/ton); S-38, Colony Shale (35 gallons/ton). For vertical scale see text.

34:S-29:S-38 in Fig. 2. Another factor that contributes to the vertical scale is the amount of samples injected for each. Even though the volume injected is held constant, the concentration of materials in each changes because of solubility, extraction efficiency, and dilution factors. A fair assessment of these influences can be obtained by collecting the chromatographic effluent for the entire run, evaporating off the eluent, and then weighing the dry material. This results in a ratio of contents of 10:14:21 for S-29:S-31:S-32 in Fig. 1, and a ratio of 20:10:20 for the three in Fig. 2. Normalizing with respect to the weight of materials collected and the instrumental factors, one should, therefore, multiply the heights of each peak (from "null") in the chromatograms by 1.0, 0.77 and 0.53 for S-29, S-31 and S-32, respectively, in Fig. 1, and by 0.58, 1.0 and 0.58 for S-34, S-29 and S-38, respectively, in Fig. 2.

The first observation is that these chromatograms are extremely rich in struc-

ture. All chromatograms have been checked with multiple injections, and reproducible results were obtained. There were drifts in the baselines due to the instabilities in the optics and the modulation, but these can be readily distinguished from the chromatographic features. The nature of the instrumentation dictates that any deviation from 'null" (baseline) can only be due to an actual rotation of the polarization, and not absorption or refractive index changes. On the other hand, the presence of optically active materials in the chromatographic effluent need not result in a measurable signal due to possible cancellation of co-eluting species. Similarly, the peak heights (from "null") may not be proportional to the concentrations. So, if anything, we may still be underestimating the amount of optically active components in the samples. The second observation is that there are dextrorotatory as well as levorotatory components in all the samples. This confirms that bulk optical activity is not a useful parameter in the characterization of the samples due to cancellation of the effects. In fact, the better the separation, the more reliable is the interpretation. The third observation is that without exception, the integrated optical activity is biased towards the dextrorotatory sense. This is consistent with the measured bulk rotatory powers of these samples[6]. It is also consistent with bulk measurements in other types of fossil fuels[3–5,7]. Presumably the skeletons of certain biological markers are more likely to survive the extreme conditions of fossilization than others, and dominate in the contributions to these measurements. The fourth observation is that the chromatograms show some dependence on the particle sizes of the shale, as illustrated in Fig. 1. The contents of the two smaller particle sizes are quite similar, except for a distinctive peak at 7.5 min for the former. The larger particle size, however, provides more features and quite different relative signal strengths for each. Most notable are additional features at 8, 9, 16, and 19 min, and the absence of a feature at 10 min. Most likely, the larger particles are heated up more slowly because of their mass, and show less cracking and thus more optical activity in the end. Similar observations for various heating rates have been reported in the bulk optical activity[6]. The two smaller particles sizes are probably not different enough in mass to show this particular effect. This indicates that uniformly small particles must be used in any studies of correlations. The fifth observation is that there are major differences among samples with different origins. This is most evident in the regions towards the beginning of the chromatograms (to 5 min) and *ca.* 12.5 min. Naturally, many more representative samples will have to be surveyed to confirm these trends. The sixth observation is that there are also many similarities among the samples with respect to the location and sign of the chromatographic peaks. If biogenic origin of these shales is accepted, one would expect certain types of chiral skeleton, such as steranes[12], phytane and pristane[13], to be more abundant than others.

In summary, we report here the first chromatograms of the optically active materials in the saturated fraction of shale oil extract. The wealth of information present suggests that these chromatograms may be good fingerprints of the shale oil, and may be useful for the characterization of fossil fuels in general.

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