Optical Rotation of Petroleums

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Abstract

Although oils and oil distillates are usually dextrorotatory, some levorotations can be measured in lower boiling distillates. Fractional distillation of a Colombian crude oil of Eocene age showed that optical rotation is maximal at an average molecular weight of 464. The rotatory power of petroleum reflects the extent to which its composition has been transformed during geochemical maturation. Optical rotations thus can be correlated with the degree of maturity in much the same way as can such other compositional features as aromatic character or content of steroid-like substances, which are demonstrable in petroleums.

The optical activity of petroleum is gradually degraded by maturational influences, and a decreasing trend in rotatory power is recognized in a comparison of oils produced from rocks of progressively greater geologic age. The optical rotation of dark crude oils can be measured in a polarimeter of suitable photometric sensitivity. The measurements extend geochemical application of oil polarimetry, which was restricted formerly to oil distillates and decolorized oils.

Introduction

ALTHOUGH THE OPTICAL ROTATION of a "naphte" was reported by Biot as early as 1835 (6), the actual identity of his sample is uncertain. Little attention was given to Biot's observation until Walden (32) resumed the work and expressed the first association between the rotatory power of petroleum and its presumed biological origin. Since that time (1906) optical activity has remained important evidence for biochemical participation in the generation of petroleum. Some attempts have been made to attribute optical activity to optically active contaminants acquired after generation and accumulation of the petroleum (17). Evidence for this interpretation is lacking, and a majority of investigators believe that optical rotations measurable in petroleums or their derivatives represent preserved residues or transformation products of biologically contributed precursors in the petroleum source materials.

The nature of the precursors to optical rotation in petroleums has remained a topic of considerable interest and speculation. Sterols are mentioned frequently in this connection because of their wide distribution in lipids, which are among the most prominent of the suspected source materials of petroleum. Historical evidence for sterol contributions to optical activity in petroleum is summarized in the reviews by Bergmann (5), Gurwitsch and Moore (12), and Louis (18). At best however, the evidence is suggestive. Fenske and others (10) measured rotations in various oil distillates and showed that optical activity is concentrated in fractions, the molecular weight of which approximates 400.

Later work by Oakwood et al. (26) indicates that the optically active substances in both a Texas and a California oil are predominantly naphthenic hydrocarbons containing four or five rings. The Texas sample yielded crystalline hydrocarbon material of high specific optical rotation (approximately +38 at 589 mμ). Generally similar findings were reported by Louis (20) in the analysis of a Texas crude oil although the melting point of his crystalline preparation was much lower. Both reports indicate that the isolated substances contain approximately 87 to 88% carbon and 12 to 13% hydrogen.

These compositions support the data of Mair, Willingham, and Streiff (22), who found that maximum optical rotation in an Oklahoma crude oil is exhibited by a fraction, the empirical formula of which is $C_{27.7}H_{52.6}$, which is purely naphthenic and contains 2.4 rings per molecule. This investigation shows also that appreciable rotation is measurable in both higher and lower boiling distillates corresponding to fractions in the range of C_{23} to C_{34}. A molecular range of this magnitude indicates that, if sterols were important contributors to the optical rotations observed, a series of smaller and larger compounds must have been generated from them during the transformation of organic matter to petroleum.

The majority of polarimetric analyses of petroleums available in the literature was conducted with distillates. The data indicate clearly that optically active materials are demonstrable over a wide range of molecular sizes. Work with oils in the USSR shows measurable rotations in fractions boiling at temperatures as low as 60–95C and extending to the highest boiling fractions tested (575–600C) (1). The data show a molecular-weight range of 380 to 480 for maximum rotation. In most instances, treatment of distillates with sulfuric acid did not affect the rotational values which were observed. This finding suggests that optical activity is not associated primarily with the presence of aromatics.

The work of Soviet chemists shows also that the greater the paraffinicity of an oil fraction, the lower is its optical rotation (23,30). By inference, then, rotation would appear to be associated with naphthenic components. Although the majority of oils and distillates are dextrorotatory, Sattar-Zade (29) showed considerable levorotation among various fractions in the 300–475C range of an Artem Island (Azerbaidzhan SSR) oil.

Louis (18) measured optical rotations in six oils from the Paris Basin. Rotation becomes evident in fractions corresponding to a molecular weight of 200 and reaches a maximum in a molecular-weight range of about 370 to 460. In later work Louis (19) showed measurable optical activity in the aromatic separates of various oils which were fractionated chromatographically. An oil from Indonesia exhibited maximum activity in the aromatic fraction and was levorotatory ($[\alpha]_D = -9.60$). The demonstrations of optical rotation over a wide range of molecular weights and the occasional appearance of levorotatory materials imply that the optical activity of petroleum probably cannot be assigned to a single precursor substance or type of substance.

Relatively little is known of the optical rotations of whole, or unfractionated, crude oils. Two conditions are responsible: a) polarimetry of petroleums of high absorbance is difficult, frequently impossible with conventional instruments; b) the net optical activity of whole crude oils often is low, and analysis is impracticable if dilution is required to overcome the problem of absorbance.

The present study takes up the polarimetry of unfractionated crude oils with new techniques of sample preparation and with an instrument of high photometric sensitivity. Data are presented also relative to the problem of steroid involvement in the optical rotation of petroleum, the distribution of optically active compounds in oils, and the relationship of optical rotation to oil maturation.

Experimental Procedure

Polarimetry

All optical rotations were measured in a Rudolph Model 200–80 photoelectric polarimeter. The original multiplier phototube and associated amplifier were discarded and replaced by units of greatly increased sensitivity. Numerous light sources were tested in order to analyze oils of high absorbance. The sources included sodium and mercury arcs, zircon and xenon concentrated arcs, and helium-neon gas lasers. The xenon arc is the most useful of the sources tested. A detailed description of the polarimeter and its development will be reported elsewhere. The precision of most measurements is ±0.005° although the instrument can be operated with a precision as high as ±0.002°. Results are reported to the nearest 0.01°. Measurements are made according to the method of symmetrical angles described by Rudolph (28).

Attention should be directed to the expression of results. The available literature on oil polarimetry indicates two conventions. One is unambiguous: observed rotation per described length of sample, e.g., $\alpha_D^{25} = +0.50°$ per decimeter of oil. The subscript indicates that the wavelength of measurement is 589 mμ, the D line of sodium light. The superscript refers to temperature in degrees C, usually reported only infrequently in petroleum analysis. Fenske et al. (10) noted that rotations of oils respond only slightly to changes in temperature. The measurements reported in the present paper were made at room temperature (22 ± 2C) and are not otherwise specified. The second method of reporting results involves a misnomer. This is the term specific rotation, or $[\alpha]$, which is calculated ordinarily from observed rotation, α, in the following manner:

$$[\alpha] = \alpha \cdot 100/l \cdot c,$$

where l is sample length in decimeters and c is concentration of the optically active compound in grams per 100 ml of solution. But the optical rotation of a petroleum is that of an unknown compound or mixture of compounds present in an unidentified concentration.

Vellinger (31) indicated the incongruity of $[\alpha]$ expressions in oil analysis; nevertheless a large proportion of literature data is reported in terms of this unit. In spite of its erroneous derivation however, use of the so-called specific rotation of oils is advantageous because it facilitates comparison of samples of considerable difference in specific gravity. The $[\alpha]$ term is therefore used in sections of the present report and is calculated by dividing observed rotation per decimeter of oil by density of sample.

Sample Preparation

Many of the measurements reported were made when photometric sensitivity of the polarimeter was inadequate for the analysis of samples of high absorbance. Fenske and coworkers (10) showed that little change in rotation is induced by passage of oil through a decolorizing clay, such as Fuller's earth. The observation is supported by demonstrated relationships between optical activity and nonpolar hydrocarbon content of petroleums. Accordingly samples were decolorized by percolation through activated alumina in the following manner.

A column, 2 cm in diameter and 15 cm in length, is packed with activated alumina (chromatographic grade, 80–200 mesh, Matheson Coleman and Bell, No. 9296). Five ml of oil are introduced into the column. The eluting solvent, *n*-hexane, is then added slowly and allowed to percolate through until 25 ml of eluate are collected. The solvent is removed from the eluate by evaporation in a hot-water bath under a nitrogen atmosphere. Oils thus recovered from eluates vary in color from water-white to light amber. A generally similar procedure was followed also by Louis (18) in his analysis of Paris Basin oils.

Oils decolorized by this procedure will show changes in $[\alpha]$ value, ranging from a few to as much as several hundred milli-degrees. When tested with oil distillate fractions, the alumina treatment shows almost no effect on rotation in the lower boiling ranges and larger effects at higher molecular weights. Net effects on whole crudes vary with types of different oils which represent various distributions of optically active components. Experimental comparisons of treated and untreated whole crude oils showed that the major portion of rotational activity was retained after passage of the oils through alumina. Some changes can occur however, and these contributed significantly to experimental error in early phases of this work. Such errors stimulated polarimeter improvement to a level of photometric sensitivity adequate to eliminate pretreatment of oils with alumina.

The alumina treatment was discontinued as soon as photometric sensitivity of the polarimeter was increased sufficiently for dark oil analysis. Some difficulty was experienced at first in poor reproducibility of results. This was traced to light scattering by suspended particles in the dark oil samples. Particle size evidently approximates colloidal dimensions, and the difficulty was overcome by the filtration of oils through membrane filters such as the millipore type. A filter pore diameter of 0.10μ is sufficient to remove the particles completely.

Filtration is facilitated if the sample is prefiltered successively through 0.45μ and 0.22μ membranes. Control analyses of oils before and after such filtration showed that the only effect of this treatment is the elimination of random variation in rotational values as a result of light scattering. Interrelationships between optical activity and light scattering have been discussed at length by several investigators (13,25,27).

Colorimetric Test for Sterol-Like Characteristics

A conventional Liebermann-Burchard reaction is produced readily with decolorized (alumina-treated) oils. Color is developed by the modified Moore and Baumann variation of the classical colorimetric method (9).

Determination of Molecular Weights

Molecular weights of oil distillates were determined by vapor-pressure depression in a Mechrolab Vapor Pressure Osmometer. Theory and operation of the vapor pressure apparatus are discussed by Brady et al. (7).

Determination of Polycyclic Hydrocarbon Concentrations

Concentrations of polycyclic hydrocarbons in oil distillates were measured with a 19-component hy-

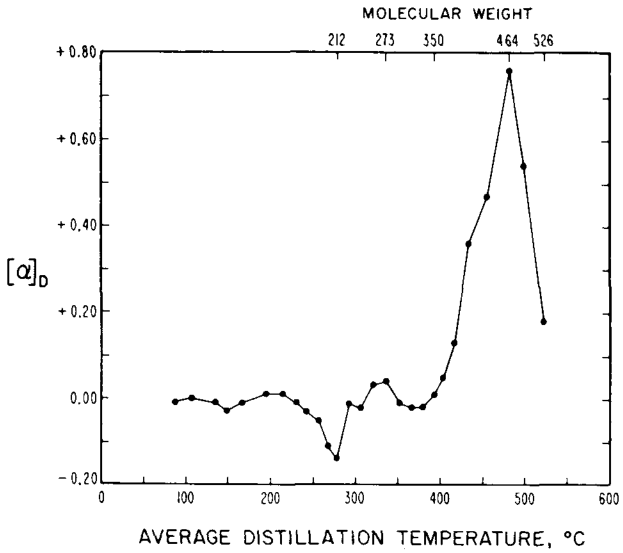

Fig. 1. Optical rotations of distillate fractions of Rio Zulia (Colombia) crude oil.

drocarbon analysis by high resolution mass spectrometry, according to the method of Gallegos et al. (11).

Results and Discussion

Rotation in Oil Distillates

An Eocene crude oil from the Lower Mirador formation in the Rio Zulia Field of Colombia was fractionated under high vacuum so that actual distillation temperatures would not exceed the cracking temperature. The oil distillates were not decolorized prior to analysis although the high absorbance of fractions boiling above approximately 400C required that such distillates be diluted with toluene. Optical rotations of the distillates are summarized in Figure 1, which indicates also the average molecular weight of the distillate of maximum rotation. The oil exhibits its greatest optical activity at an average molecular weight of 464. This value is compatible with the presence of polycyclic structures.

The curve shows also the relatively wide distribution of levorotatory materials. The broad spectrum of molecular sizes over which optical rotation is measurable and the existence of both dextrorotatory and levorotatory components argue against the concept of a single precursor or class of precursors that confer optical activity upon petroleums. The pronounced maximum in rotation occurs however in a molecular-weight region which could be associated with compounds derived from a steroid, terpenoid, or similar source-material.

Effects of Oil Maturation

Optical rotations have been measured in a large number of unfractionated oils. Figure 2 compares rotations in alumina-treated oils with oil aromaticity as indicated by a ratio of aromatic to paraffinic infrared absorbance.[1] In spite of considerable scatter, the data show that the degree of optical rotation normally increases with the increasing aromaticity of oil. Highly asphaltic oils frequently exhibit large dextrorotations. Values ($[\alpha]_D$) of +1 to +5 are not uncommon in heavy asphaltic petroleums. Such oils will show high aromatic to paraffinic ratios, but the persistence of pronounced optical activity after treatment of the oil with activated alumina or with sulfuric acid, as reported by others, indicates that the saturated rather than the aromatic fraction is associated with optical rotation. The assignment of maximum optical rotation to a molecular-weight region of 400 or higher and the obvious association of high optical activity with asphaltic oils imply that polycyclic structures may be sources of rotatory compounds in petroleums.

If optical activity is most pronounced in heavy asphaltic oils, it should be possible to observe some correlation of rotatory power with geologic age. Evidence indicates that a heavy asphaltic character is typical of geochemically immature petroleum, i.e., petroleum in which large complex structures are still relatively intact (3,24). Prolonged geothermal exposure of such structures results in a gradual breakdown of large polycyclic compounds with a corresponding formation of smaller molecules (16). If this reaction concept is operable, it suggests that increasing maturation should reflect a decreasing optical rotation.

In addition to such decreases reported in the present paper, similar changes were noted by others (2,3). Figure 3 displays the optical rotations of oils recovered from sedimentary deposits of known geologic age. Although only a limited number of measurements are available, the highest degree of optical activity is concentrated among oils from younger rocks. The

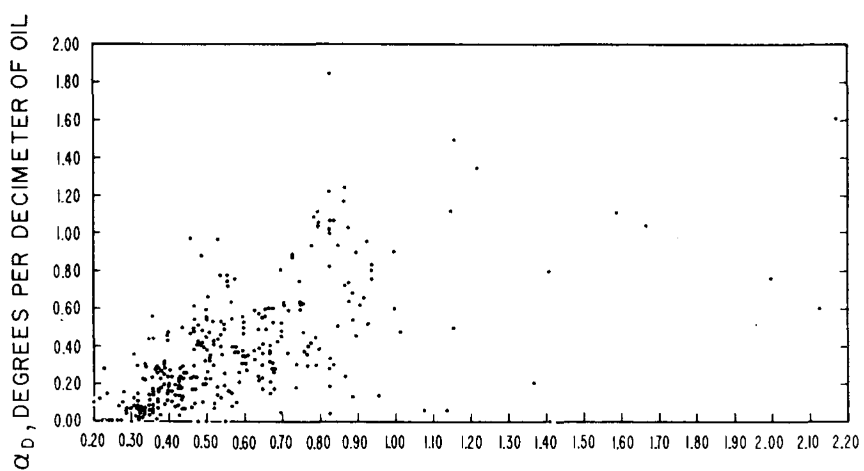

Fig. 2. Optical rotations of oils of various compositions.

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[1] The ratio is measured prior to treatment with alumina and is determined from absorbance (A) measurements according to the formula

$$\text{Ratio} = (A_{6.25\mu} + A_{12.35\mu} + A_{13.50\mu} + A_{14.55\mu})/4(A_{13.80\mu})$$

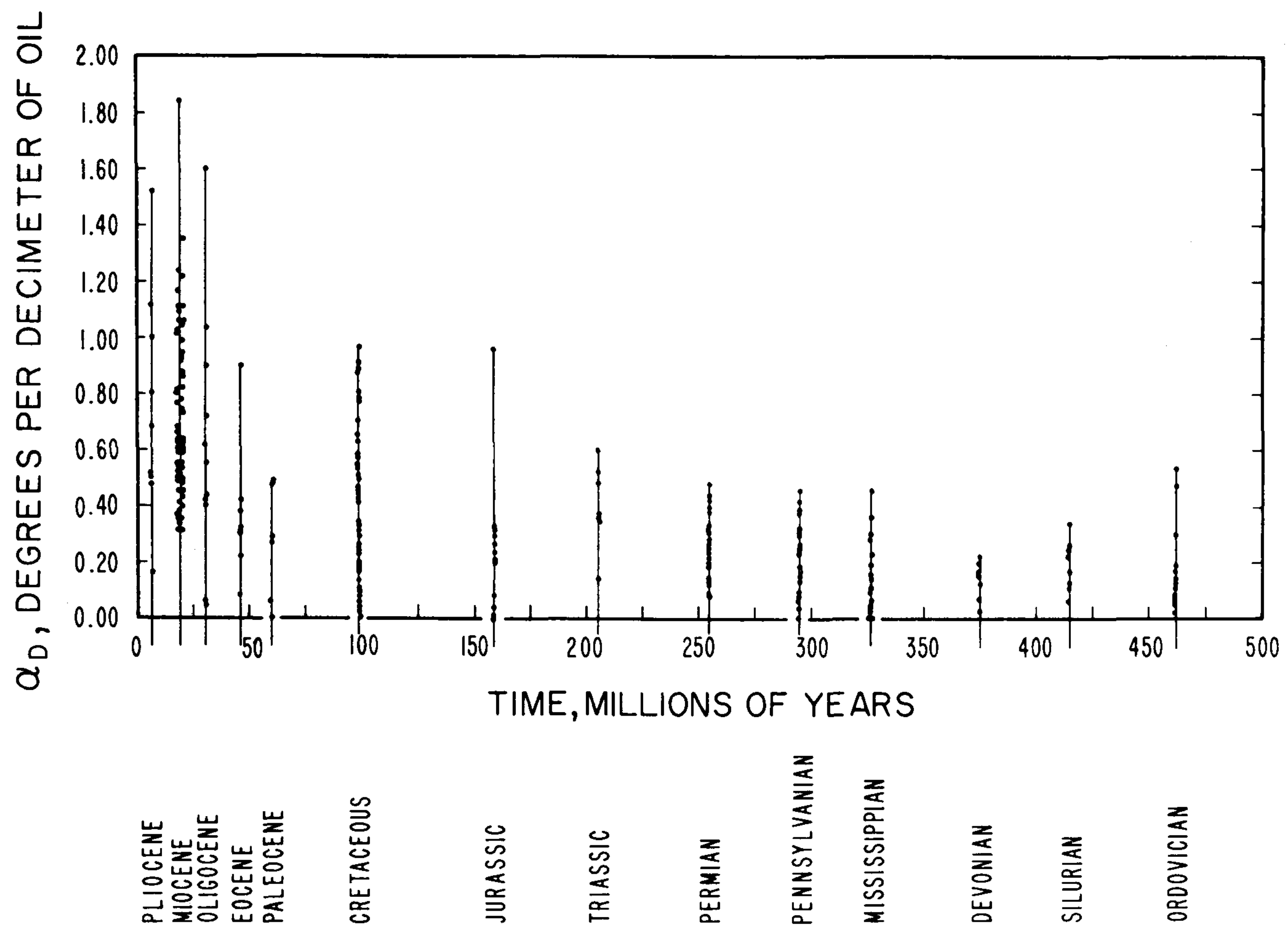

FIG. 3. Optical rotations of oils produced from rocks of various geologic ages.

picture unquestionably is complicated by the inclusion of oils which may have migrated to their present positions from source rocks of different ages.

Optical Rotation and Sterol-Like Materials in Oils

Early workers were impressed by various evidences for an association of the optical rotation of petroleum with the presence of sterols or sterol transformation products (5). Sterol-like material is readily demonstrable in petroleums. Indeed, positive Liebermann-Burchard reactions suggestive of steroids are exhibited by many oils from a variety of sources. The intensity of the color reaction, referred ordinarily to absorbance at 620 mμ, is related generally to the state of geochemical maturity characteristic of the oil in question. Reaction reaches a maximum in the asphaltic crude oils that show such other evidences for immaturity as high optical rotation and large aromatic-to-paraffinic ratios.

Figure 4 presents the apparent correlation between Liebermann-Burchard reaction and optical rotation in several oils from various locations. Oils were decolorized prior to both analyses. The data are not intended to identify Liebermann-Burchard reacting substances with optically active materials although such an identification may become possible when the reacting materials are concentrated or separated from the oils. In any case, the use of an artificial standard (cholesterol) for colorimetric determination of sterol-like material shows such apparently high concentrations ($>3\%$) that generation solely from sterol sources is questionable.

Other sterol color reactions, such as the Salkowski, can be demonstrated also. Additionally, oils will frequently precipitate insoluble complexes when treated with the saponin digitonin. Precipitated digitonides can be separated from the oils and reacted with Liebermann-Burchard reagents to yield the classical color reaction. Although digitonide formation is typical for sterols, such precipitation is not specific for these compounds.

Mair (21) reviewed a considerable amount of evidence for the role of terpenoids as precursors to various petroleum hydrocarbons. The extent to which such hydrocarbons might contribute to steroid reac-

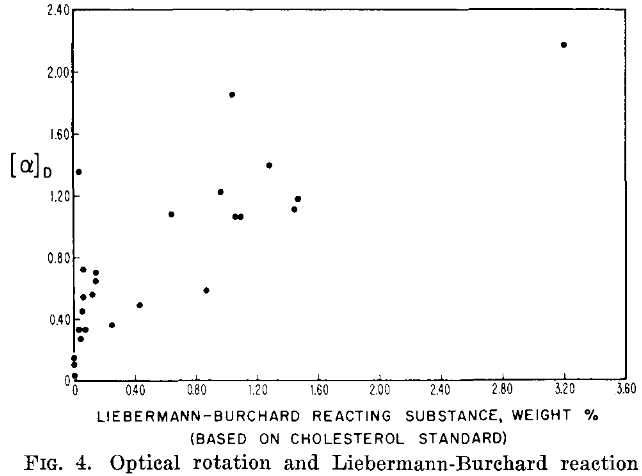

FIG. 4. Optical rotation and Liebermann-Burchard reaction for sterols in crude oils.

tions of oils is not known. The widespread occurrence of sterol-like substances in petroleums may also be associated with the presence in oils of steranes, triterpanes, and similar compounds. Several compounds apparently derived from plant triterpenoids have already been isolated from high-boiling fractions of petroleums (4,14). Burlingame et al. (8) reported the isolation and identification of C_{27}-, C_{28}-, and C_{29}- steranes and a C_{30}- pentacyclic triterpane from the branched-cyclic alkane fraction of the Green River Shale.

Hills and Whitehead (14,15) found high concentrations of tetracyclic and pentacyclic naphthenes in a Nigerian crude oil distillate boiling at 478C. Optical rotation of the Nigerian oil increases to a maximum in the same distillate and then diminishes progressively in higher boiling fractions. These data agree with the Rio Zulia (Colombia) oil analyses reported above. Rio Zulia distillates show maximum optical rotation in the fraction boiling at about 480C. Both tetracylic and pentacyclic hydrocarbon concentrations were found to be high in this fraction although these compounds reach their maximum at somewhat higher boiling points. These relationships are shown in the following tabulation.

Rio Zulia distillate, mean boiling point	$[\alpha]_D$	Saturated Hydrocarbons, weight %	
		Four-ring	Five-ring
434C	+0.36	3.1	1.5
454.5	+0.47	3.7	2.5
480.5	+0.76	4.3	4.6
499	+0.54	5.1	4.6
521.5	+0.18	4.0	4.7
557.5	Not measured	3.8	5.0
579+	Not measured	3.4	2.3

These data reinforce earlier suggestions about the involvement of polycyclic naphthenes as contributors to the optical rotation of petroleums. No information is presently available about the relationship of such compounds to the sterol-like color reactions of crude oils.

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