STUDIES ON PETROLEUM
WITH THE ULTRACENTRIFUGE

Paul A. Witherspoon

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PAUL A. WITHERSPOON

ABSTRACT

The question of whether or not colloidal particles exist in petroleum has long been a fundamental problem. There is a lack of unequivocal evidence and often a confusion of conflicting statements in the literature.

An apparently new approach to this problem is the use of the ultracentrifuge to impose a gravitational force field sufficient to separate colloidal particles from petroleum. Extensive studies have been carried out with the ultracentrifuge on one Mississippian crude oil from the Illinois basin, and additional work has been done on samples of a Pennsylvanian and a Devonian oil from the same basin. A California crude oil of Pleistocene age also has been studied briefly.

Prolonged centrifugation of the Mississippian oil has demonstrated that at least three different groups of colloidal particles are dispersed in the oil. One group that has been separated from the oil is an organic sediment and has been identified as asphaltenes. Analytical centrifugation work indicates that the density of these asphaltene particles is 1.22 g/cm^3. Assuming that the asphaltene particles are spherical and that the degree of solvation is not an appreciable factor, the average particle size is calculated to be 40 Å. Similar results were obtained with the other two Illinois oils. It is suggested that 40 Å may be a unit particle dimension for the asphaltenes. A molecular weight of 30,000 was obtained for this material.

Less specific data are given for the nature of the other two groups of colloidal particles that were segregated within the Mississippian oil but not separated from it. A method of isolating these fractions for more quantitative study is proposed.

The occurrence of discrete asphaltene particles in these three Illinois crude oils is consistent with the fact that Illinois oils generally are somewhat asphaltic. The important implication, however, is that, because asphaltic materials are commonly present in petroleum, practically all crude oils contain colloidal particles. The results of this work indicate that crude oil contains several different groups of colloids.

In addition to the organic sediment that was centrifuged from the Illinois crude oils, a very minor amount of inorganic sediment also was obtained. Electron micrographs of this material revealed a significant amount of clay particles. Although no organic sediment could be centrifuged from the California crude oil because of its extremely high viscosity, it yielded significantly more inorganic sediment than did the Illinois oils. The inorganic sediment from the California crude contained a substantial amount of clay-like particles. It is postulated that investigations of these clay materials and of the various groups of organic colloids in crude oil may provide important information on the genesis of petroleum.

Use of the ultracentrifuge thus provides an important new approach to fundamental research on the nature of petroleum.

INTRODUCTION

This report demonstrates the application of ultracentrifugal techniques to the isolation and study of the colloidal components in petroleum. The ultracentrifuge apparently has not heretofore been applied to petroleum, and the results of these investigations suggest that this new approach may have considerable merit.

PREVIOUS RELATED RESEARCH

Petroleum is an exceedingly complex mixture of hydrocarbons and minor amounts of inorganic compounds. Entire books (Gruse and Stevens, 1942; Sachanen, 1945) have been devoted to its chemical technology. About one-fourth of the material in the six-volume treatise, *The Science of Petroleum*, is concerned with the nature of crude oil.

After 27 years of investigation in API Research Project 6, Rossini and co-workers have isolated and identified 141 different hydrocarbons from just one Oklahoma crude oil, representing about 44 percent of the original sample (Rossini and Shaffer, 1954). They report paraffin hydrocarbons ranging from methane (CH_4) through eicosane ($C_{20}H_{42}$) and large groups of alkyl cyclopentanes, alkyl cyclohexanes, and alkyl benzenes.

In recent years the application of infrared and mass spectroscopy has provided a means of examining the heavier constituents of crude oil. Such investigations have revealed the presence of complicated ring systems "to a degree which substantiates other evidence that the most numerous of molecules comprising crude oil are ring systems with numerous alkyl substituents" (Stevens, 1956, p. 52).

If the nature of petroleum seems involved, the intriguing problem of its origin is even more so. Many investigators have studied petroleum genesis, but the complicated nature of crude oil and the fact that the point of entrapment may be at some distance from the point of origin have raised a number of difficult questions. As might be expected in such a complex problem, the theories proposed have been varied and often conflicting. Rather than review the many theories that have evolved in the past half century, I shall summarize briefly only the modern ones.

Substantial and convincing evidence supports the theory of an organic origin for petroleum. The most important such discovery was the identification by Treibs (1934a, 1934b) of measurable quantities of organically derived porphyrins in a large number of samples of bituminous shale, petroleum, ozocerite, and natural asphalts from all over the world. Porphyrins are derived either from chlorophyl in plants or hemoglobin in animals.

The original source materials may be either land-derived (Haseman, 1921; Berl, 1938; Efendiev, 1954; Corbett, 1955) or marine (Emery and Rittenberg, 1952). These materials are generally deposited in shallow marine facies (Trask and Patnode, 1942; Weeks, 1952; Smith, 1954) although deposition in a lacustrine environment has been reported (Hunt et al., 1954). Bacterial action is responsible for the initial processing of the organic material, but whether such action can produce hydrocarbons other than methane remains unanswered (Stone and Zobell, 1952).

The reported presence of liquid hydrocarbons in soils (Swain and Prokopovich, 1954) and in recent marine sediments (Smith, 1954) is not necessarily proof that conversion to crude oil occurs rapidly, because these hydrocarbons differ in kind from those of recognized source beds and petroleum itself (Hunt and Jamieson, 1956; Stevens et al., 1956). There is some evidence that would indicate the transformation of organic matter passes through a youthful stage of heavy asphaltic oils, which are further altered by low-temperature physico-chemical processes to a mature paraffinic stage (Barton, 1934, 1937; Bornhauser, 1950; Tamrazyan, 1954; Karimov, 1955). Such reactions appear to be a function of time and temperature (McNab et al., 1952) and very probably are catalyzed by certain minerals in the sediments, of which the clays may be the most active (Gruse and Stevens, 1942, p. 255; Grim, 1947; Brooks, 1952). As might be expected, the final petroleum product is probably dependent upon the type of source materials as well as the environment of deposition (Weeks, 1952; Hunt et al., 1954), and very likely there is more than one mode of formation (Stevens, 1956).

Research on petroleum has necessarily been confronted with the important question of whether particles of colloidal dimensions (10 to 5000 Å) occur in oil. If such particles are present, they must be intimately involved with the other petroleum constituents and, by the very nature of colloidal systems, one would expect the physical and chemical properties of the oil to be influenced significantly. Thus, one would anticipate that a knowledge of the colloidal components in crude oil should be of great assistance to research on the nature of petroleum. As crude oil is apparently the product of a series of trans-

formations to the final mature, paraffinic stage, it seems likely that any colloidal components would also be affected by such transformations. Inasmuch as samples of crude oil may be obtained over a wide range of geologic ages (Pleistocene to Cambrian) as well as a wide range in depths, an investigation of the colloidal components in petroleum might provide important information on the question of genesis.

This knowledge would also be important in petroleum recovery and utilization because colloidal fractions in crude oil are likely to contain the more complex and polar compounds. The presence of such compounds in petroleum has already been established, as will be revealed in the following discussion. The natural occurrence of crude oil within the heterogeneous system of a reservoir rock is always intimately associated with water. Thus, the above compounds will be the ones concentrated at the interfaces in the system, thereby affecting the wettability of the solid phase as well as the interfacial phenomena between oil and water phases. Because of the enormous internal surface of sedimentary rocks, interfacial forces are magnified in their effect and may therefore be expected to play an important part in the multi-phase flow of oil and water through porous media. This would affect both the initial accumulation of petroleum and its subsequent exploitation.

Reisberg and Doscher (1956) in studying the displacement of crude oil (Ventura field, California) by water in saturated cores, have recently reported that oil recovery was dependent not only on lowering the interfacial tension between the displacing water and the oil but also on overcoming rigid interfacial films that developed at oil-water interfaces and caused the oil to adhere to a water-wetted, hydrophilic surface. The interfacially active materials in the Ventura crude oil were isolated and found to be asphaltic materials. Babalyan and Kuliev (1956) have reported that the displacement of water by crude oil is strongly controlled by polar compounds in petroleum.

Another practical problem of the petroleum industry is the handling of oil field emulsions. These may be either oil-in-water or water-in-oil suspensions, but the latter are more commonly encountered. Emulsions may be thin and mobile or they may be so viscous that they must be handled as solids. In either case, the oil phase is not readily available, and a tremendous amount of study has been devoted to the problem of breaking such dispersions to recover the oil.

In an early study, Lottermoser and Calantar (1929) reported that asphaltic materials lead to the formation of stable water-in-oil emulsions. Morrell and Egloff (1931) have summarized the properties of emulsions and methods of breaking them, and Uren (1939, p. 483-520) has presented a detailed discussion on this subject. These workers also suggest that asphaltic materials in crude oil act as the principal emulsifying agent by forming a rather stable film around water droplets. When these droplets are brought into contact, they seem to resist coalescence, and, if mechanically distorted, tend to subdivide into smaller droplets (Morrell and Egloff, 1931, p. 505). Lawrence and co-workers (1948, 1954) have shown that emulsions of sea water in fuel oil were caused by very stable asphaltic films. Morrell and Egloff state that at times asphaltic material may be separated by filtration, leaving an oil which does not emulsify, and they interpret this as an indication that such materials are in a colloidal state in the oil.

As a result of such practical considerations, there has been considerable interest in recent years in the problem of isolating polar, or surface-active, constituents from petroleum and investigating their properties. Bartell and Niederhauser (1949) initiated this work by isolating film-forming materials of asphaltic character from crude oil obtained in the Rio Bravo field, California. Solutions of these materials were not found to contain colloidal particles when examined by an ultramicroscope or in ultrafiltration experiments using collodion films with pore sizes of about one micron. They suspected that exposure to

oxygen during the sampling procedure had something to do with the production of surface-active materials, and therefore examined ten other oils in the absence of air and found little if any film-forming constituents. They concluded that such materials are not normally present in oil reservoir fluids. Denekas et al. (1951) also have isolated film-forming materials from an Oklahoma City crude oil that they identified as high-molecular weight normal paraffins of 50 to 80 carbons per molecule. They postulated that these heavy aliphatics might exist in the oil as finely dispersed wax crystals stabilized by a protective colloid.

Dodd et al. (1952) investigated the same two crude oils studied by the workers mentioned above and a third sample from the Lagunillas field of Venezuela. They adopted a different approach by analyzing for trace metal constituents and found vanadium, iron, magnesium, calcium, nickel, titanium, and copper (more or less in descending order of magnitude). They also isolated surface-active constituents and found that they contained trace metals. Only part of the metallic constituents was identified in these film-forming materials, however, which suggests that metals occur in petroleum in more than one kind of molecular form, or at least in a range of molecular sizes. Although inconclusive, their results support the assumption that film-forming constituents in petroleum consist of mixtures of a number of organically-derived materials of which porphyrins and their metal complexes are interfacially the most active. They suggest that the conclusion of Bartell and Niederhauser (1949) that film-forming substances do not exist in the reducing environment of a petroleum reservoir should be re-examined.

An important contribution to this problem has subsequently been reported in a very thorough investigation by Dunning (1953) and co-workers (1953, 1954). They studied a heavy asphaltic crude oil from the North Belridge field, California, and definitely established that vanadium and nickel porphyrin complexes were the major contributors to the interfacial activity

and film-forming tendencies exhibited by this sample. Some of the porphyrin-metal complexes that they isolated, however, were interfacially inactive.

Spectrophotometric measurements indicated metal contents in the oil of 0.0028 percent vanadium, 0.0080 percent nickel, and 0.0025 percent iron. In addition, qualitative spectrochemical analyses revealed the presence of sodium, calcium, magnesium, and traces of titanium and lithium. Their work also corroborates the findings of Dodd et al. (1952) in that not all of the nickel and vanadium was complexed with porphyrin molecules. Since the porphyrin compounds are generally quite stable, these materials should be expected to be interfacially active in the oil reservoir.

It is interesting to note that none of the above workers mentioned the presence of colloidal-sized particles in the crude oils studied. In fact, in the literature on the presence of such particles in petroleum, there is a lack of unequivocal evidence and often a confusion of conflicting statements. For example, in an early symposium on colloid chemistry, Dunstan (1931) mentions, as evidence of the colloidal nature of petroleum, the waxes that are known to be associated with paraffinic oils, the coagulation of bituminous materials from asphaltic oils, the optical heterogeneity of oil, and the ability of surface-active materials such as fuller's earth to decolorize hydrocarbons. Morrell and Egloff (1931, p. 503) in this same symposium reiterated Dunstan's views and summarized their thinking with the statement, "It is quite obvious to one with even a superficial knowledge of the subject that petroleum . . . . . ., especially the asphaltic base types, is a colloidal system."

On the other hand, Gurwitsch (1931, p. 523), in this same symposium, presented different views. He stated that the scattering of light by oil is only weakly polarized, and therefore the reported optical effects (as of 1931) are due to the well-known fluorescence of petroleum rather than scattering by colloid particles. With regard to the precipitation of asphaltic materials from oil, Gurwitsch pointed out that large proportions of solvent are necessary, so that

the effect may simply be one of a change in solvent with resultant ordinary precipitation. In discussing the reported presence of colloidal wax in petroleum, he stated that from his own observations a number of paraffin-base oils of widely different origin "show an abundance of paraffin crystals when examined microscopically in polarized light" (Gurwitsch, 1931, p. 524).

After discussing the meager work that had been done on osmosis, diffusion, and cataphoresis of oil, Gurwitsch concluded that the properties generally characteristic of the colloidal state are only very indefinitely developed in petroleum. Freundlich (1938) supports the viewpoint of Gurwitsch, although he is inclined to suspect that colloidal particles are present but are too elusive to be found. Eckert and Weetman (1947) have reported Brownian movement for benzene solutions of asphaltic materials, but dialysis experiments with these solutions leave only minor portions of the asphaltic substance that do not pass through a collodion membrane.

With the advent of the electron microscope some 15 years ago, Preckshot et al. (1943) looked for colloidal-sized asphaltic particles in crude oil without success. When untreated crude oil was examined, no particles could be seen. If some solvent such as benzene or petroleum ether were added to the oil, however, particles as small as 100 Å appeared, which Preckshot et al. attributed to a precipitation phenomenon caused by the solvent. Using a Sharples supercentrifuge, they were able to obtain small amounts of asphaltic substances after short periods of centrifugation. The amounts obtained, however, were much smaller than the total asphaltic content of the oil, and they considered the results unsatisfactory.

By applying an electrical potential to the crude oil or by causing it to flow through a porous media so as to develop a streaming potential, they precipitated a significant amount of asphaltic material of colloidal size. In the case of electrodeposition, the sediment collected on the positive electrode, indicating particles of negative charge. Preckshot et al. considered electrical

effects responsible for the formation of the colloidal particles in both cases. From these negative results, they concluded that either colloidal particles are not present in the crude oils studied, or they are too small to be seen.

Katz and Beu (1945) subsequently tried to use improved techniques with the electron microscope and investigated gilsonite (a natural asphalt), a manufactured asphalt, and an asphaltic crude oil from the Greeley field in California. No colloidal particles could be found in any of these hydrocarbons unless they were treated with some solvent, in which case asphaltic particles as small as 100 Å were observed, as in the previously described work of Preckshot et al. In checking the resolving power of their microscope, they concluded that particles as small as 32 Å could be seen. From hundreds of observations on their samples, they concluded that colloidal particles, if present in natural petroleum or asphalt, are less than 65 Å in diameter. They postulate that perhaps these systems contain "potential colloids" that are easily converted to colloidal solutions either by addition of the proper solvents or from electrical effects. More recently, Skinner (1952) was equally unsuccessful in observing discrete particles in untreated crude oil from the Santa Maria Valley field in California.

Although the above reported research has failed to find colloidal-sized particles in asphalts or crude oils, there seems to be no doubt in the minds of the investigators of asphalt that they are dealing with a colloidal system. The first elaborate colloid-chemical investigation on asphaltic bitumen was reported by Nellensteyn (1923). Out of this and subsequent work have come two general terms: *maltenes,* which is that portion of an asphalt that is soluble in aromatic-free gasoline or diethyl ether, and *asphaltenes,* the insoluble portion. The maltenes can be further fractionated into resins, oil, and wax. Asphaltenes are black, solid, noncrystalline substances that when heated do not soften but decompose and finally sinter together.

At atmospheric temperatures, asphalts are highly viscous and sometimes apparently solid. They are available naturally or may be produced from petroleum by several methods that essentially amount to a process of condensation or precipitation. Their rheological properties vary considerably, but extensive studies of these properties have led to the conclusion that asphalt is a colloidal system (Eilers, 1949).

The general concept of this system is that the asphaltenes are the centers of micelles, with the various materials known as maltenes adsorbed on the surfaces of the asphaltene particles. According to Pfeiffer and Saal (1940) the structure of the micelle is such that the substances with the greatest molecular weight and most pronounced aromatic nature form the nucleus. Around this nucleus are arranged lighter and less aromatic constituents, and there is a gradual transition to preponderantly aliphatic compounds (see fig. 1). In other words, there is no distinct interface either within the micelle or between it and the surrounding environment.

According to this view, Pfeiffer and Saal (1940) theorize that when the entire system contains sufficient constituents for the formation of the outer regions of the micelle, the asphaltenes are fully peptized and able to move through an asphalt as freely as the viscosity of the matrix permits. If there is a shortage of the maltene fractions, however, part of the adsorptive forces that cause the formation of the micelle are not compensated, and there will be a condition of mutual attraction. The micelles will form a kind of bond when they accidentally approach each other closely enough to get into a region of minimum potential energy resulting from a counterbalance of attractive and repulsive forces.

If this same concept holds for asphaltic particles in petroleum, the action of precipitants apparently removes part of the peptizing layers of the maltenes, although other reasons for precipitation have been proposed (Nellensteyn, 1931; Kalichevsky, 1938). In the dispersed state, the micelles in asphalt are believed to be essentially spherical in shape (Pfeiffer and Saal, 1940;
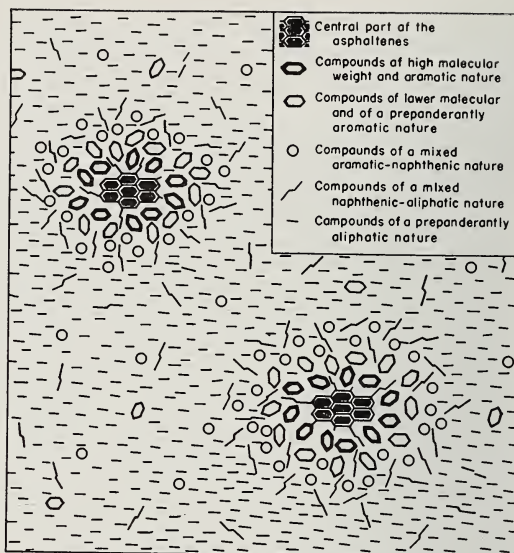
FIG. 1.—Concept of the structure of asphaltene micelle. (After Pfeiffer and Saal, 1940.)

Höppler, 1941) although deviations from a sphere may occur with increasing concentration (Eilers, 1949).

If asphalt is accepted as a colloid system, one is inclined to suspect that petroleum should be too. For example, the asphaltic material separated from crude oil has distinct colloidal properties, and Freundlich (1938, p. 1057) considers it improbable that precipitation of these materials by hydrocarbon solvents should produce any chemical change in the substance precipitated. On the other hand, very careful electron microscopy has failed to find discrete particles in either crude oil or in asphalt. Perhaps the micelle concept of Pfeiffer and Saal (1940) provides an explanation. If there is no definite interface between the micelle and its environment as they suggest, then the dispersed particles do not provide a reflecting surface to beams of light or electrons (Freundlich, 1938; Skinner, 1952). Undoubtedly, these particles, if they do exist as such in petroleum, are quite small, which further complicates the problem.

One approach to this problem is the use of the ultracentrifuge to impose a gravitational field sufficient to cause any particles of colloidal dimensions to separate from

their environment. In such an approach there must be a difference in densities between the particle and its dispersing medium, otherwise no driving force will be present to cause particle movement. Most crude oils range in specific gravity from 0.8 to 0.95, and the gravity of asphaltenes is reported to be much higher, exceeding 1.0 (Sachanen, 1945, p. 405). A search of the literature indicated that this approach has never been investigated. As mentioned previously, Preckshot et al. (1943) used centrifugation on crude oil briefly but did not consider their results satisfactory.

It was decided that the modern techniques that have been developed in ultracentrifugation might be applied to crude oil. The chief purpose of this research has been to explore this idea and to present some rather limited results to demonstrate the usefulness of the method.

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I also should like to thank Dr. H. N. Dunning of the Bureau of Mines, Bartlesville, Oklahoma, for samples of vanadium and nickel porphyrins from his laboratory and a sample of California crude oil on which he has done much investigation; Mr. Richard W. Love of The Texas Company for crude oil samples obtained in the Salem Consolidated field; and Mr. R. A. Wilson of the Tidewater Oil Company for the samples obtained in the Main Consolidated field.

This report is taken from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Geology in the Graduate College of the University of Illinois, 1957.

EXPERIMENTAL DETAILS

Crude Oils Investigated

Extensive studies were carried out on one Mississippian crude oil taken from a well drilled to the Benoist sand at a depth of 1,805 feet in the Salem Consolidated field. This well is known as the Salem Unit, W. A. Sands No. 3 in SE¼ NW ¼ SW¼ sec. 33, T. 2 N., R. 2 E., Marion County, Illinois. Additional work was done on a Devonian crude oil taken from a well drilled to the Devonian limestone in the same field at a depth of 3,362 feet. This second well is known as Salem Unit, McYoung Heirs No. 39 in SW¼ NE¼ SW¼ sec. 20, T. 2 N., R. 2 E., Marion County. Samples of both oils were obtained in air as well as under an atmosphere of nitrogen as described later. The wells are operated by The Texas Company.

A sample of a Pennsylvanian crude oil that was collected in air from a well drilled to the Robinson sand at a depth of 946 feet in the Main Consolidated field also was studied. This well is located in W½ SW¼ of sec. 18, T. 13 W., R. 7 N., Crawford County, Illinois, and is operated by the Tidewater Associated Oil Company.

Dr. H. N. Dunning of the U. S. Bureau of Mines, Bartlesville, Oklahoma, very kindly provided a sample of a heavy, viscous, asphaltic, crude oil from California. This oil was obtained (presumably in air) from the Tulare sand (Pleistocene age) at a depth of 760 feet on the Gibson lease operated by the Union Oil Company of California in the North Belridge field, Kern County (Dunning et al., 1953).

A summary of available data from the Illinois State Geological Survey files on the physical properties of these crude oils is given in table 1.

Collection of Crude Oil Samples

Crude oil samples were collected in air in two-quart Mason jars by attaching a

Crude Oil	Gravity–60/60°F		Viscosity-centipoise				Color
	A.P.I.	Sp.Gr.	50°F	77°F	100°F	130°F	
Pleistocene *	14.1	0.972	—	—	1050	322	Black
Pennsylvanian	37.2	0.839	8.6	5.3	4.0	—	Black
Mississippian	36.1	0.844	10.2	5.7	4.0	—	Black
Devonian	38.2	0.834	9.7	5.5	3.9	—	Greenish black

*Data from Dunning et al. (1953).

short length of small rubber hose through appropriate connections to a 1-inch gate valve normally present at the wellhead of any producing well. After the sample line was connected, the gate valve was first opened to determine how much oil and water were being produced and to purge the line. If the water-oil ratio was above approximately 1.0, the produced fluids were first collected in a glass separator and the water drained off, after which the oil was poured directly into the sample bottle. If the water-oil ratio was less than 1.0, the produced fluids were collected directly in the sample bottle. All sample bottles were covered with aluminum sheet foil and the metal cap screwed on. Occasionally it was necessary, depending on atmospheric temperatures, to loosen the cap and vent any natural gas that had been released. The crude oils were stored in these containers until investigated.

Special glass apparatus was built to collect crude oil samples under an atmosphere of nitrogen at the producing well. The apparatus consisted of a 1-liter cylindrical, separatory funnel on which additional glass stopcocks were sealed. This apparatus was filled with nitrogen and produced fluids were admitted directly, after which any water could be discarded and the sample kept under positive pressure. The atmosphere above the samples was usually a mixture of the original nitrogen in the apparatus and any natural gas released from the oil. Samples were stored in the apparatus until investigated, and positive pressures were maintained during storage by adding nitrogen as necessary. Normally

this was required only when a drop in temperature occurred. Details of the sampling procedure are given in Appendix A.

PREPARATIVE CENTRIFUGATION PROCEDURE

Crude oil collected in air was poured directly into the lusteroid tubes of a No. 30.2 angle-head rotor and centrifuged for varying lengths of time at 30,000 r.p.m. (or 80,000 G) and approximately 20°C. in a Model L Spinco preparative centrifuge manufactured by Specialized Instruments, Inc.

For crude oil that had been collected under a nitrogen atmosphere, the special apparatus used for collecting the samples in the field (see Appendix A) was modified slightly so that the centrifuge tubes could be filled in an atmosphere of nitrogen. Details of the procedure are given in Appendix B. Centrifugation experiments were carried out at the same speed and temperature as mentioned above.

At the end of any centrifugation run, the crude oil was poured off and the tubes were allowed to drain upside down for ten minutes. After this draining period, the tube with sediment was weighed to the nearest milligram. This weight, compared with the tared weight of the empty tube, gave an indication of the amount of sediment collected. After being weighed, the sediment was dispersed in either benzene or carbon tetrachloride.

As might be expected, an appreciable amount of crude oil adhered to the inside surfaces of the centrifuge tube after the draining period. To evaluate the magnitude of this oil film, clean centrifuge tubes

were filled with the various crude oils, and the film was measured by weighing the centrifuge tube, both empty and after draining. The results of several measurements on the three Illinois crude oils are summarized in table 2. Because of the extremely high viscosity of the California crude oil, this unusual oil could not be handled in this fashion.

TABLE 2.—CRUDE OIL RETAINED ON INSIDE SURFACE OF CENTRIFUGE TUBES AFTER DRAINING TEN MINUTES (ROOM TEMPERATURE, 24 TO 25°C.)

Crude Oil	No. tubes examined	Grams of oil per tube	
		Range	Average
Pennsylvanian	5	0.022–0.023	0.023
Mississippian	3	0.020–0.022	0.021
Devonian	5	0.021–0.028	0.024

In some of the experiments the various layers of oil in the centrifuge tube were removed separately in order that analyses could be carried out on each portion. The usual methods of sampling were not satisfactory when applied to viscous oil. Therefore, the technique of freezing the crude oil with liquid nitrogen was utilized. A metal holder was designed to support eight tubes while they were being lowered into liquid nitrogen in a Dewar flask. In the freezing operation, the centrifuge tube was lowered into the liquid nitrogen about $1/2$ to 1 cm. at a time. Lowering the tube in this manner, minimized any mixing due to thermal gradients from the cold exterior of the tube to the relatively warm interior. After the tube and contents were frozen solid, segments were obtained by placing a single-edge razor blade on the tube and striking a sharp blow.

ANALYTICAL CENTRIFUGATION PROCEDURE

The nature of the sediments obtained in the preparative centrifugation experiments was further investigated by study of dispersions in benzene and carbon tetrachloride in the analytical centrifuge. These runs were carried out at 60,000 r.p.m. (or 250,000 G) at temperatures of around 23° C.

and using a Model E Spinco ultracentrifuge manufactured by Specialized Instruments, Inc. The usual operating procedures were followed; these are not discussed here because details are generally available in technical manuals or in the literature. A Type A rotor and a 4-millimeter deep cell with plane quartz windows were used. This shallow cell was used to increase light transmission through the relatively dark solutions.

It was not possible to use the refractive index gradient method for following a sedimentation boundary because the indices of refraction of the solution and of the solvent were so close together that practically no refractive peak could be detected. Therefore, it was necessary to utilize the light absorption method of Svedberg and Pedersen (1940). Light of a certain wave length and of constant intensity is sent through the quartz-windowed cell and a number of exposures are taken at intervals on a photographic plate, or film, with the camera focused on the cell. If sedimentation occurs, the sedimenting particles will leave behind a relatively clear solution through which more light is transmitted than through the original solution. Thus, one observes a gradual clarification that can be recorded photographically. The rate of sedimentation is determined by making a series of exposures during the course of a run. The method of analyzing these exposures is explained in more detail under the topic, "Analytical Centrifugation to Characterize Crude Oil Sediment."

In using the light absorption method, it is necessary to have what is known as a "concentration scale." This is obtained by filling the cell successively with a series of known concentrations of the particular solution to be studied. With the centrifuge running at experimental conditions, initial exposures of each concentration are taken at several different exposure times. After the exposed plates are developed, the percentage of light transmission of each exposure can be measured. Comparison of the results permits selection of the most desirable exposure time for the concentration under investigation.

It is assumed in this procedure that when the light density and exposure time have been kept constant, a given concentration in the cell will always give rise to the same blackening intensity on the plate. Therefore, it is possible by use of the concentration scale to obtain the concentration in an analytical centrifugation run at any point in the cell. As the 50-percent concentration position is the center of the sedimentation boundary (Svedberg and Pedersen, 1940, p. 7) it is possible to measure sedimentation rates directly.

In these experiments the concentration scale for benzene solutions of Mississippian sediment was obtained in the following manner. The sediment was dispersed at concentrations of 0.1, 0.4, 0.8, 1.0, 1.4, and 1.8 mg/ml. Each of these solutions was centrifuged in the 4 mm. analytical cell with exposures being made at 5, 10, 20, 40, and 60 seconds. Each exposed film was developed for three minutes in the same fresh developing solution. The light transmission was measured for each exposure with a model MM-102 Spec-Reader densitometer manufactured by National Spectrographic Laboratories. The results are summarized in table 3.

The data of table 3 are plotted in figure 2 which shows more clearly the relation between light transmission and concentration for any given exposure. It will be noted that the 20-second exposure curve is essentially linear up to a least 1.4 mg/ml. concentration. As it is highly desirable in

the light-adsorption method to have such a linear relationship, 20-second and occasionally 25-second exposures were used throughout this work. Concentrations were kept between 1.0 and 1.4 mg/ml., although this was difficult to control exactly because there generally was a varying amount of crude oil that accompanied the sediment.

The Spec-Reader densitometer was not equipped with a calibrated scale to indicate the movement of the rack. Therefore, the mechanical drive that moves this rack was calibrated in the following manner. A long photographic plate was marked on the gelatin side with a scratch about 25 centimeters in length, which was approximately the length of the film being measured. Six separate marks were made at right angles to this scratch at about 4-centimeter intervals, and the distances between each mark were determined with a cathetometer.

They were then measured three times on the densitometer by counting the number of turns of the wheel that operates the mechanical drive. The light transmission slit of the densitometer was used as a reference and was simply moved from mark A to B, etc., and the number of turns recorded. From these measurements, it was determined that the distance moved by the rack was approximately 0.02 cm. per turn of the drive wheel. The maximum difference between the lowest and highest values obtained was 0.00005 cm. per turn, or an apparent variation in the linearity of the mechanical drive of only 0.25 percent. On

TABLE 3.—LIGHT TRANSMISSION DATA FOR ESTABLISHING CONCENTRATION SCALE
(MISSISSIPPIAN SEDIMENT DISPERSED IN BENZENE)

Analytical Run*	Conc., mg/ml.	Average percentage transmission for exposures†				
		5 sec.	10 sec.	20 sec.	40 sec.	60 sec.
A–1871	1.8	93	93	90	83	68
A–1872	1.4	92	92	87	65	41
A–1873	1.0	88	80	60	30	18
A–1874	0.4	80	60	23	7	1
A–1875	0.1	60	30	8	2	0
A–1876	0.8	88	82	56	23	12

*Assigned numbers refer to permanent file numbers of film negatives and data sheets in Ultracentrifuge Laboratory, University of Illinois.
†All readings refer to an arbitrary setting of 100 on lightest negative.
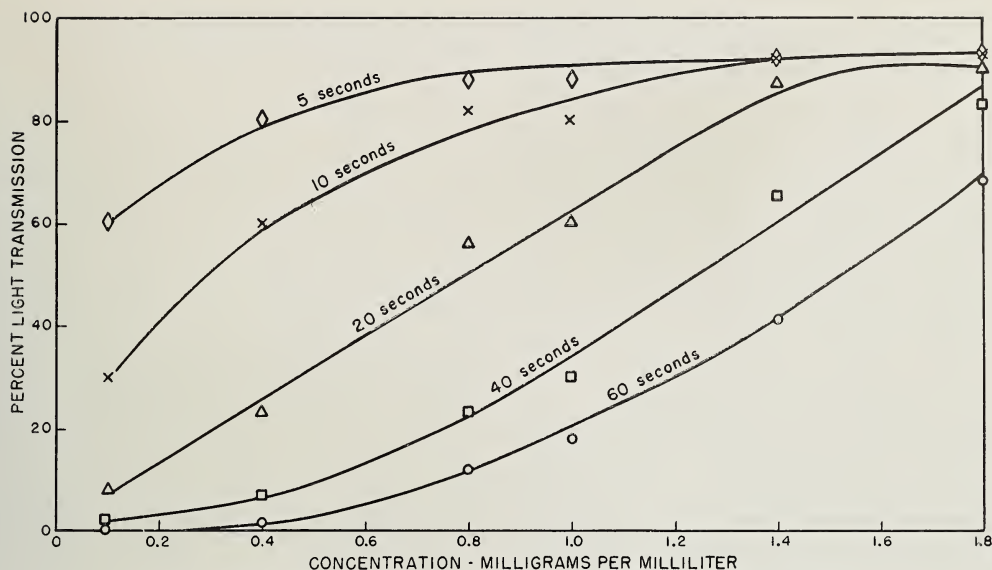
Fig. 2.—Concentration scale for Mississippian sedimentation in benzene.

the basis of these measurements, the arithmetic average value of 0.02111 cm. per turn was used in converting densitometer readings to distances on the film negatives.

SPECIFICATIONS OF SOLVENTS

Specifications of the various solvents used in this work are given in table 4.

TABLE 4.—SPECIFICATIONS AND SOURCE OF SOLVENTS

Solvent	Source	Specifications
Benzene	Allied Chem. & Dye Corp.	Purified, 99–100%
Benzene*	Allied Chem. & Dye Corp.	ACS reagent grade, thiophene free
Carbon tetra-chloride	Allied Chem. & Dye Corp.	CP, boiling range 75°–77°C.
Chloroform	Allied Chem. & Dye Corp.	ACS reagent grade, approx. 0.75% ethyl alcohol
Ethyl alcohol	U. S. Industrial Chem. Co.	USI-USP absolute
Ethyl ether	Mallinckrodt Chem. Works	Analytical reagent grade
n-Pentane	Phillips Petroleum Co.	Pure grade, 99 mol% minimum
n-Heptane	Phillips Petroleum Co.	Pure grade, 99 mol% minimum

*Used in interfacial tension measurements.

EFFECT OF COMPRESSIBILITY ON SEDIMENTATION RATES

As discussed previously, benzene, carbon tetrachloride, and mixtures of the two were used as dispersing agents in analytical centrifugation studies on the crude oil sediments. Both solvents have significant coefficients of compressibility, and consequently their densities and viscosities show an appreciable increase with pressure. The effects of compressibility on sedimentation rates were therefore evaluated.

Unfortunately, the literature on the effect of compressibility on sedimentation rates is very limited. Most analytical centrifugation has been performed with aqueous solutions, and because of the relatively low compressibility of water, it is standard procedure to neglect compressibility effects. In the case of nonaqueous solutions, however, these effects may be quite significant. Svedberg and Pedersen (1940, p. 37-38) discuss the necessity for evaluating the effect of increased densities and viscosities due to compressibility, but they do not treat the subject analytically.

Mosimann and Signer (1944) have presented a method of correcting for the compressibility of acetone, but their approach results in a correction factor that could not

conveniently be used in this work. Jullander (1945) in working with acetone has used their correction factors. Others (Gralen, 1944; Newman and Eirich, 1950; Newman et al., 1953) in working with a variety of nonaqueous solutions of nitrocellulose have not mentioned compressibility effects. In view of the general lack of literature on this subject, a fundamental approach was adopted in arriving at correction factors readily applicable to the data of this investigation.

Sedimentation in Benzene

The effect of compressibility for dispersions of low concentration may be conveniently approached from a modification of the well known Stokes' law. In the case of sedimentation in a sectorial cell of an analytical ultracentrifuge, the acceleration due to gravity is replaced by that of the imposed centrifugal field so that Stokes' equation becomes

$$\frac{4}{3} \pi r^3 (d - d_m) w^2 x = 6 \pi v r \frac{dx}{dt} \quad (1)$$

Here

$r =$ radius of sedimenting particle, cm.

$d =$ density of particle, g/cm.³

$d_m =$ density of dispersing medium, g/cm.³

$w =$ speed of rotation, radians/sec.

$x =$ distance of particle from center of rotation, cm.

$v =$ viscosity of dispersing medium, poise

$\dfrac{dx}{dt} =$ instantaneous sedimentation velocity of particle at point x along direction of imposed centrifugal field, cm/sec.

Equation 1 may be rearranged to

$$dt = \frac{4.5}{r^2 w^2} \cdot \frac{v}{d - d_m} \cdot \frac{dx}{x} \quad (2)$$

and if the ratio $\dfrac{v}{d - d_m}$ is essentially constant, which is the case when compress-

ibility effects are negligible, equation 2 is readily integrated from the form

$$\int_{t_1}^{t_2} dt = \frac{4.5}{r^2 w^2} \cdot \frac{v}{d - d_m} \int_{x_1}^{x_2} \frac{dx}{x} \quad (3)$$

When compressibility must be considered, both v and d_m become functions of x as a consequence of the hydrostatic pressures developed in the rotating system, which vary from zero at the surface of the liquid to a maximum at the bottom of the cell. If we can assume that the effective density of the particle, d, does not change as a result of its changing environment, which is a reasonable first approach, equation 2 becomes

$$\int_{t_1}^{t_2} dt = \frac{4.5}{r^2 w^2} \int_{x_1}^{x_2} \frac{v_x \, dx}{(d - d_{mx}) x} \quad (4)$$

Equation 4 can be solved if the pressure at any distance below the meniscus of the solution is known and if the variations of density and viscosity with pressure are known.

For a compressible liquid, it can be shown (see Appendix C) that, when there is an essentially linear relationship between density and pressure (which is the case for benzene and carbon tetrachloride up to at least 500 atm.), the pressure in a rotating system can be calculated from

$$P_x = \frac{d_i}{m} \left(e^{\frac{m w^2 (x^2 - x_i^2)}{2.026 \cdot 10^6}} - 1 \right) \quad (5)$$

where

$P_x =$ pressure (above atmospheric) at distance x from center of rotation, atm.

$d_i =$ density of liquid at meniscus, g/cm.³

m = slope of the linear variation be-
tween density and pressure,
g/cm.³ atm.

x_i = distance from center of rotation
to meniscus, cm.

Equation 5 requires density data for various pressures at some specific temperature. As temperatures in the analytical centrifugation work reported here varied from 22.4°C. to 25.6°C. and averaged 23.5°C., a temperature of 23°C. was arbitrarily selected. It can be shown (see Appendix D) that at this temperature the density of benzene varies with the pressure as

$$d_{mx} = 6.714 \cdot 10^{-5} P_x + 0.8752 \qquad (6)$$

Therefore, in equation 5, m = $6.714 \cdot 10^{-5}$ g/cm.³ atm. and d_i = 0.8752 g/cm.³.

In solving equation 5 it is convenient to use a fixed value of x_i, the distance from the center of rotation to the meniscus. Actually x_i varied from 5.81 to 5.93 cm. in various experiments and averaged 5.89 cm. An arbitrary value of 5.9 cm. was therefore adopted, although x_i could be assumed to be 5.8 or 6.0 cm. without introducing any significant effects.

It is also convenient to use a constant speed of rotation. With the speed control on the Spinco ultracentrifuge set at 59,780 r.p.m., the speeds varied from 59,700 to 59,798 r.p.m. and averaged about 59,750 r.p.m., which was consequently adopted.

To determine pressures at various distances from the meniscus, arbitrary increments of 0.1 cm. were chosen in equation 5 along with the average data mentioned above (table 5). It was then a simple matter, using equation 6, to obtain the effective densities summarized in table 5.

It is also necessary to have the variation of viscosity with distance from the meniscus, and the following formula (see Appendix E) can be used for benzene at 23°C:

$$\log \frac{v_x}{0.00622} = 0.3575 \cdot 10^{-3} P_x \qquad (7)$$

where v_x = viscosity at point x. Calculated values of viscosity are included in table 5.

TABLE 5.—CALCULATED PRESSURES AND RESULTING DENSITIES AND VISCOSITIES WITH BENZENE IN ANALYTICAL CENTRIFUGATION CELL*

x, cm.	Dist. from meniscus, cm.	P_x, atm.	d_{mx}, g/cm³	v_x, poise
5.9	0.0	0.0	0.8752	0.00622
6.0	0.1	19.4	0.8765	0.00632
6.1	0.2	40.2	0.8779	0.00643
6.2	0.3	61.1	0.8793	0.00654
6.3	0.4	81.9	0.8807	0.00665
6.4	0.5	104.3	0.8822	0.00678
6.5	0.6	126.1	0.8836	0.00690
6.6	0.7	148.7	0.8852	0.00703

*Pressures calculated from equation 5 assuming t = 23°C., x_i = 5.9 cm., d_i = 0.8752 g/cm³, m = $6.714 \cdot 10^{-5}$ g/cm³ atm. and a speed of 59,750 r.p.m.

To solve equation 4, it is necessary to know d, the effective density of the dispersed particles. As will be discussed later, the first approximation obtained for d was 1.25 g/cm.³ and this was used in evaluating compressibility effects. A subsequent and more accurate estimate of d gave 1.22, but as will be demonstrated, this difference is not significant.

It is convenient to assume that sedimentation starts from the position of the meniscus at zero time. From an experimental standpoint, a finite length of time is actually required to reach the desired speed of rotation, during which time some sedimentation occurs. The theoretical starting time can be determined, if desired, by extrapolating the experimental data versus time back to the position of the meniscus. On this basis, equation 4 becomes

$$\int_0^t dt = t = \frac{4.5}{r^2 w^2} \int_{5.9}^x \frac{v_x \, dx}{(d - d_{mx}) \, x} \qquad (8)$$

where t = time for sedimentation boundary to move through the compressible medium from the meniscus (x_i = 5.9 cm.) to the position x.

As densities and viscosities for benzene are known for various values of x (table 5), the integral in equation 8 can be evaluated for this solvent by numerical methods as outlined in Appendix F. The values of the integral are summarized in table 6. To compare these results with what would occur if the viscosity and density of the benzene did not increase from their values at the meniscus (that is, no compressibility), equation 3 was evaluated in a similar way, and the results are included in table 6.

TABLE 6.—CORRECTION FACTORS FOR BENZENE COMPRESSIBILITY AT 59,750 r.p.m. AND 23°C.

x, cm.	Dist. from meniscus, cm.	$\int_{5.9}^{x} \dfrac{v_x\,dx}{(d-d_{mx})x}$ *	$\int_{5.9}^{x} \dfrac{v_i}{(d-d_{mi})} \dfrac{dx}{x}$ †	Correction factor F ‡
5.9	0.0	0	0	1.00000
6.0	0.1	0.0002817	0.0002789	1.00009
6.1	0.2	0.0005643	0.0005532	1.00037
6.2	0.3	0.0008483	0.0008231	1.00083
6.3	0.4	0.0011335	0.0010886	1.00146
6.4	0.5	0.0014203	0.0013500	1.00228
6.5	0.6	0.0017091	0.0016073	1.00327
6.6	0.7	0.0020000	0.0018607	1.00445

*From equation 4 assuming d = 1.25 g/cm³.
†From equation 3 where v_i and d_i are constant and refer to meniscus values.
‡F · log x (experimental) = log x (corrected).

It may be possible to integrate equation 8 rigorously if the f (x) for v and d_m are not too complicated. Even when a linear relationship with x is assumed, however, the integration is somewhat involved, and numerical methods were therefore adopted.

The customary procedure in analyzing sedimentation velocity data is to plot log x versus t which, as equation 3 indicates, should give a straight line if compressibility is negligible. The slope of this straight line is then used to calculate the sedimentation coefficient. When compressibility is appreciable, however, a plot of log x versus t will produce a curve lying below the straight

line for no compressibility.* This may be shown on figure 3 by plotting log x versus the calculated integral values listed in table 6. Since the term $4.5/r^2w^2$ is the same constant in both equations 3 and 4, this is equivalent to plotting log x versus tk_1, where k_1 is the constant, $r^2w^2/4.5$.

It is evident from figure 3 that plotting log x (experimental) versus t for sedimentation in benzene can introduce an error if no corrections are made. Since the curvature is small, other experimental variations are likely to give enough spread in the individual points so that the curvature will not be perceptible. Thus, one will be inclined to draw the best straight line through the experimental data. If that were done over the full length of the lower curve, the slope would be about 7 percent lower than that of the upper straight line, which is an indication of the magnitude of the errors involved if corrections for compressibility are not made. Obviously this error will be reduced if the data are taken closer to the meniscus. In the present investigations, the experimental values usually extended ½ to ⅔ of the way along the curves of figure 3.

Correction factors can be computed in several ways, but it is convenient to calculate a factor for any given distance from the meniscus that will raise the lower curve on figure 3 to coincide with the upper straight line. This was done by dividing log x (corrected) by log x (experimental) at each given value of the integral (which is proportional to a given time, t). Values of F are included on table 6 and are plotted versus distance from the meniscus in figure 4. The experimental log x values must be multiplied by the appropriate factor in order to correct them to what they would be if benzene were incompressible.

As stated previously, the first approximation for the density of the dispersed particles was 1.25 and this was used in calculating correction factors. Later d was found to be nearer 1.22, and so the question arose as

*The curve will generally lie below; however, it is possible for the reverse to be true depending on the conditions and upon whether sedimentation or flotation occurs.
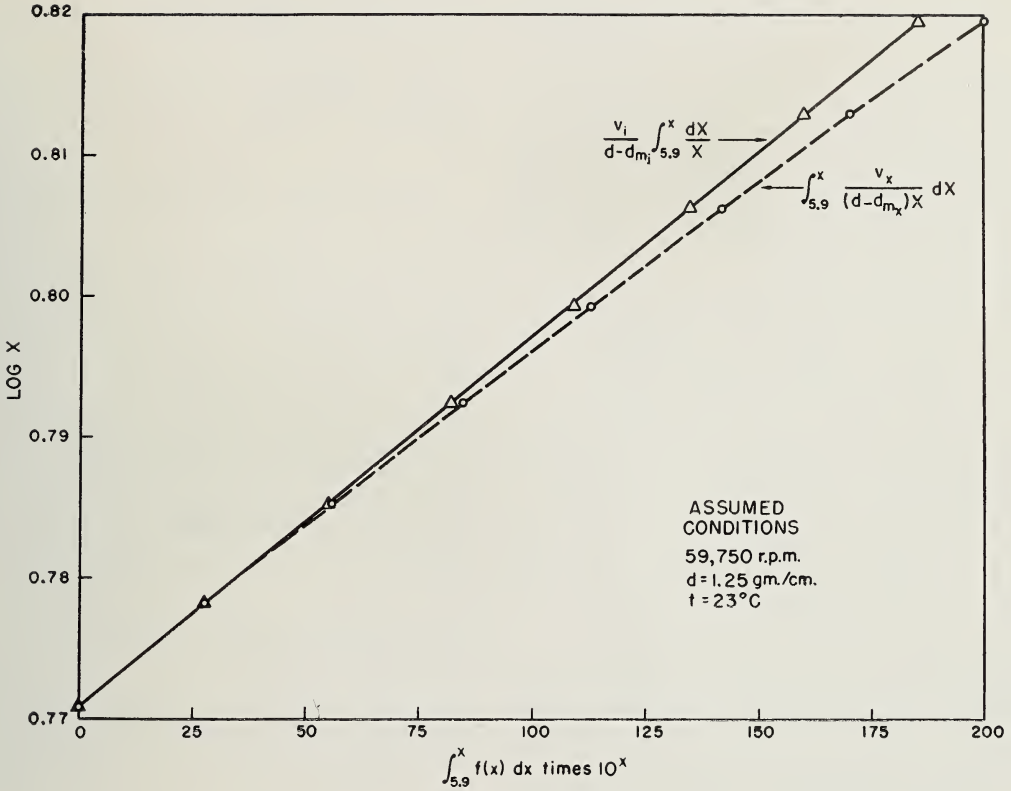
FIG. 3.—Effect of compressibility on sedimentation in benzene. (For 10^x read 10^5.)

to what effect this would have on the correction factors. Following the same procedure outlined above, correction factors were recalculated for $d = 1.22$, and the results are compared with those of table 6 in table 7. It is apparent that the correction factors are essentially identical.
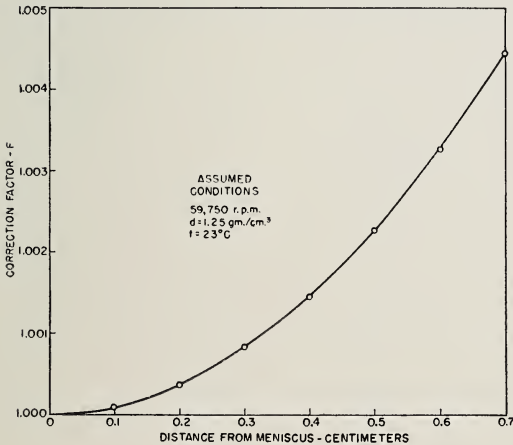
FIG. 4.—Correction factors for sedimentation in benzene.

TABLE 7.—EFFECT OF VARIATION IN DENSITY OF DISPERSED PARTICLES ON CORRECTION FACTORS FOR SEDIMENTATION IN BENZENE

x, cm.	Dist. from meniscus, cm.	Correction factor, F	
		$d = 1.25$	$d = 1.22$
5.9	0.0	1.00000	1.00000
6.0	0.1	1.00009	1.00009
6.1	0.2	1.00037	1.00037
6.2	0.3	1.00083	1.00085
6.3	0.4	1.00146	1.00150
6.4	0.5	1.00228	1.00233
6.5	0.6	1.00327	1.00335
6.6	0.7	1.00445	1.00454

Sedimentation in Carbon Tetrachloride

The equations that apply to sedimentation in benzene also hold for carbon tetrachloride, except that in the latter case flotation occurs because the dispersed particles are lighter than the solvent, and the initial limit of integration must therefore be the bottom of the cell. Equation 3, neglecting compressibility, becomes

$$\int_0^t dt = \frac{4.5}{r^2 w^2} \cdot \frac{v_1}{d_{m1} - d} \int_x^{7.2} \frac{dx}{x} \quad (9)$$

and equation 4 becomes

$$\int_0^t dt = \frac{4.5}{r^2 w^2} \int_x^{7.2} \frac{v_x d_x}{(d_{mx} - d) x} \quad (10)$$

The bottom of the cell was taken to be 7.2 cm., the average of several measurements.

Again assuming $t = 23°C.$, the variation of density with pressure may be calculated (see Appendix G) from

$$d_{mx} = 1.3788 \cdot 10^{-4} P_x + 1.5882 \quad (11)$$

from which, $m = 1.3788 \cdot 10^{-4}$ g/cm.³ atm. and $d_i = 1.5882$ g/cm³. Assuming an average speed of 59,750 r.p.m. and $x_i = 5.9$

cm., pressures were calculated using equation 5 and the results are shown in table 8. The variation of viscosity with pressure at 23°C. may be calculated (see Appendix H) from

$$\log \frac{v_x}{0.00928} = 0.3926 \cdot 10^{-3} P_x \quad (12)$$

From the calculated values of P_x, d_{mx} and v_x were determined from equations 11 and 12, respectively, and the results are included in table 8. On the basis of these data and the assumption that $d = 1.25$ g/cm.³, equations 9 and 10 were solved by the same procedure outlined for benzene. The correction factors for flotation in carbon tetrachloride are given in table 8. A plot of this factor versus distance from the bottom of the cell is given in figure 5.

Sedimentation in Mixtures of Benzene and Carbon Tetrachloride

As will be discussed later, one analytical centrifugation experiment was carried out with sediment dispersed in a mixture of two parts benzene and one part carbon tetrachloride by volume. As the density of the dispersed particles is greater than that of the mixture, the procedure discussed above for benzene was repeated.

For this mixture, the variation of density at 23°C. with pressure may be calculated

Table 8.—Correction Factors for Carbon Tetrachloride Compressibility
at 59,750 r.p.m. and 23°C.

x, cm.	Dist. from bottom, cm.	P_x, atm.	d_{mx}, g/cm³	v_x, poise	Correction factor F^*
5.9	1.3	0.0	1.5882	0.00928	
6.6	0.6	269.1	1.6253	0.01183	0.98926
6.7	0.5	310.4	1.6310	0.01228	0.99062
6.8	0.4	353.2	1.6369	0.01276	0.99214
6.9	0.3	397.4	1.6430	0.01328	0.99384
7.0	0.2	441.7	1.6491	0.01383	0.99572
7.1	0.1	487.4	1.6554	0.01441	0.99776
7.2	0.0	533.1	1.6617	0.01502	1.00000

*$F \cdot \log x$ (experimental) = log x (corrected).
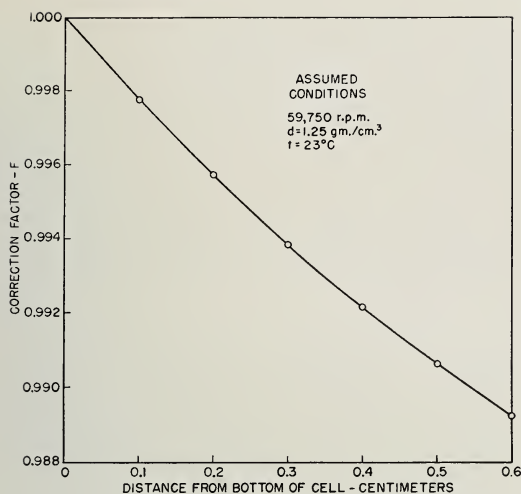
FIG. 5.—Correction factors for flotation in carbon tetrachloride.

(see Appendix I) from

$$d_{mx} = 0.9072 \cdot 10^{-4} P_x + 1.1135 \quad (13)$$

from which, $m = 0.9072 \cdot 10^{-4}$ g/cm.³ atm. and $d_i = 1.1135$ g/cm.³. The variation of viscosity with pressure at 23°C. may be calculated (see Appendix I) from

$$\log \frac{v_x}{0.00705} = 0.3691 \cdot 10^{-3} P_x \quad (14)$$

Assuming an average speed of 59,750 r.p.m. and $x_i = 5.9$ cm., pressures were calculated using equation 5, and d_{mx} and v_x were determined (table 9) from equations 13 and 14 by the same procedure outlined for benzene. The corresponding fac-

tors were computed and are summarized in table 9 and are plotted in figure 6.

One analytical run also was carried out with sediment dispersed in a mixture of one part benzene plus two parts carbon tetrachloride by volume. Because the density of the dispersed particles is less than that of the mixture, the procedure discussed above for carbon tetrachloride was repeated.

The variation of density with pressure at 23°C. for this mixture may be calculated (see Appendix J) from

$$d_{mx} = 1.143 \cdot 10^{-4} P_x + 1.3510 \quad (15)$$

from which, $m = 1.143 \cdot 10^{-4}$ g/cm.³ atm. and $d_i = 1.3510$ g/cm.³.

The variation of viscosity with pressure at 23°C. may be calculated (see Appendix J) from

$$\log \frac{v_x}{0.00807} = 0.3809 \cdot 10^{-3} P_x \quad (16)$$

Assuming an average speed of 59,750 r.p.m. and $x_i = 5.9$ cm., pressures were calculated using equation 5, and d_{mx} and v_x were determined from equations 15 and 16. The bottom of the cell was again taken as 7.2 cm., and $d = 1.25$ g/cm.³ for the dispersed particles. From these data the corresponding correction factors were computed, and the results are summarized in table 10 and plotted in figure 7.

It will be noted that these correction factors for flotation are greater than 1.0, whereas, those for flotation in pure carbon

TABLE 9.—CORRECTION FACTORS FOR 2:1 MIXTURE OF BENZENE AND CARBON TETRACHLORIDE

x, cm.	Dist. from meniscus, cm.	P_x, atm.	d_{mx}, g/cm³.	v_x, poise	Correction factor $F*$
5.9	0.0	0.0	1.1135	0.00705	1.00000
6.0	0.1	25.7	1.1158	0.00720	1.00017
6.1	0.2	51.9	1.1182	0.00736	1.00071
6.2	0.3	78.4	1.1206	0.00753	1.00163
6.3	0.4	105.6	1.1231	0.00770	1.00293
6.4	0.5	132.9	1.1256	0.00788	1.00459
6.5	0.6	161.0	1.1281	0.00806	1.00666

*$F \cdot \log x$ (experimental) $= \log x$ (corrected).
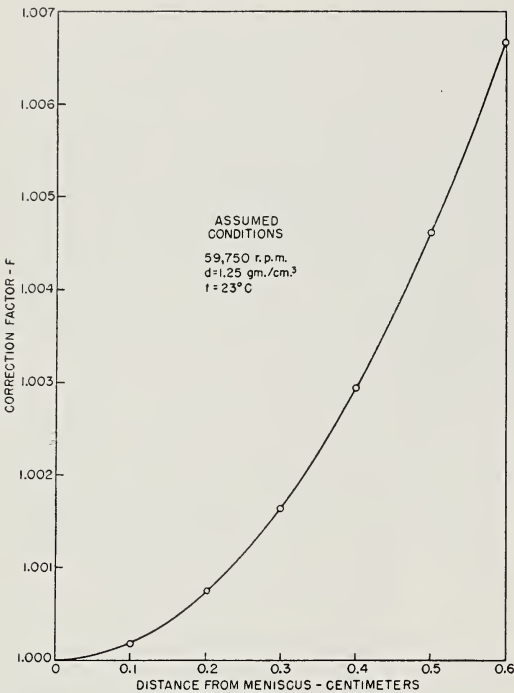
Fig. 6.—Correction factors for sedimentation in 2/3 benzene plus 1/3 carbon tetrachloride.

tetrachloride were less than 1.0. Basically, the reason for this is that in flotation the dispersed particles move from more to less dense media, which retards sedimentation, and from more to less viscous conditions, which aids sedimentation. Thus, the two effects tend to cancel each other. In the case of carbon tetrachloride the predominating effect was the reduction in viscosity,

and in the case of the above mixture, the density of the medium was close enough to that of the dispersed particles that reduction in the density term $(d_{mx}-d)$ was more significant than the reduction in viscosity.

EXPERIMENTAL STUDIES ON CRUDE OIL AND SEDIMENT OBTAINED BY CENTRIFUGATION

PRELIMINARY INVESTIGATIONS

Sediment Centrifuged from Crude Oils

In the absence of previous ultracentrifugation work on crude oil, it was necessary at the beginning of this investigation to proceed on a more or less trial and error basis. Several preliminary preparative centrifugation experiments were performed on the Mississippian and Devonian oils. After one hour of centrifuging samples at 30,000 r.p.m., a small amount of a black, tar-like sediment was found at the bottom of the centrifuge tubes. In the case of the Mississippian oil, weight measurements indicated about 0.3 percent of the oil was sedimented; the accumulation from the Devonian oil was considerably less.

The crude oils in this first experiment were separated from the sediment and centrifuged in a second step for 15 hours at 30,000 r.p.m. Approximately the same results were obtained as before, indicating that there might still be more sediment suspended in the oil. Therefore, a third run

TABLE 10.—CORRECTION FACTORS FOR 1:2 MIXTURE OF BENZENE AND CARBON TETRACHLORIDE

x, cm.	Dist. from bottom, cm.	P_x, atm.	d_{mx}, g/cm.³	v_x, poise	Correction factor F*
5.9	1.3	0.0	1.3510	0.00807	
6.7	0.5	266.0	1.3814	0.01019	1.00099
6.8	0.4	302.1	1.3855	0.01052	1.00070
6.9	0.3	338.5	1.3897	0.01086	1.00049
7.0	0.2	375.9	1.3940	0.01122	1.00030
7.1	0.1	414.3	1.3984	0.01161	1.00013
7.2	0.0	452.9	1.4028	0.01201	1.00000

*F · log x (experimental) = log x (corrected).
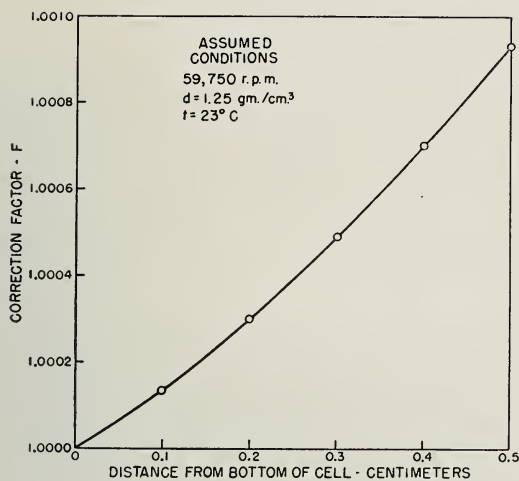
FIG. 7.—Correction factors for flotation in 1/3 benzene plus 2/3 carbon tetrachloride.

of 29 hours at 30,000 r.p.m. was made. It revealed that an appreciable amount of sediment had again been centrifuged from the Mississippian oil although an insignificant amount was obtained from the Devonian sample. On the basis of these experiments, it was concluded that preparative centrifuge runs should be at least 2 days in length. As the sediment obtained from the Devonian oil was less than that from the Mississippian, it was decided to concentrate most of the detailed investigations on sediment centrifuged from the latter crude oil.

Preparative Centrifugation of Heptane-Oil Mixtures

Preliminary investigations were made on mixtures of normal heptane and the Mississippian crude oil. The heptane-to-oil ratios used were: 0.5, 1.0, 10, and 100 by volume. After 46 hours of centrifuging at 30,000 r.p.m., a comparison of the amounts of sediment was made. The data are summarized in table 11, and it may be seen that heptane enhanced sedimentation. One factor was undoubtedly the reduction in viscosity produced by the addition of heptane. It also was likely that some precipitation and/or aggregation of colloidal particles resulted, at least at the higher dilutions. However, the percentage of sediment obtained with heptane ratios of 0.5 and 1.0 was the same as the maximum amount obtained in longer runs on straight oil (see fig. 8). Also, the results in table 11 for heptane ratios of 10 and 100 are very rough approximations because of the small weights involved.

In this preliminary investigation on heptane-oil mixtures, a curious color banding was noted in those tubes in which the heptane-to-oil ratio was 0.5 and 1.0. The banding disappeared in about a half hour from the time the centrifuge run ended. This curious effect was investigated further in subsequent experiments and will be discussed in more detail later.

TABLE 11.—COMPARISON OF SEDIMENT CENTRIFUGED FROM MISSISSIPPIAN OIL AND MIXTURES OF NORMAL HEPTANE AND OIL

No. tubes	Average oil per tube, gm.*	Heptane-to-oil volume ratio	Sediment plus oil film gm.†	Oil film gm.	Average sediment per tube	
					gm.	% of oil
4	7.686	0	0.083	0.021‡	0.062	0.8
2	5.201	0.5	0.103	0.008**	0.095	1.8
2	3.820	1	0.071	negligible	0.071	1.9
2	0.700	10	0.029	negligible	0.029	4††
2	0.074	100	0.005	negligible	0.005	7††

*Calculated from total weight of mixture in tube and densities of n-Heptane (0.675 g/cm³.) and of oil (0.844 g/cm³.) assuming additive mixing.
†After draining 10 minutes. Room temperature, 23° to 24°C.
‡See table 2.
**Average value obtained after draining mixture for 10 minutes from four unused tubes.
††Because of small amount of oil involved, this is only a rough estimate.

TABLE 12.—COMPARISON OF SEDIMENT CENTRIFUGED FROM MISSISSIPPIAN CRUDE OIL
COLLECTED IN AIR AND IN NITROGEN*

Collected in	No. of tubes	Average oil per tube, gm.	Sediment plus oil film per tube†		Oil film, gm.‡	Average sediment per tube	
			Range, gm.	Avg., gm.		gm.	% of oil
Air	9	7.85	0.099–0.114	0.108	0.021	0.087	1.1
Nitrogen	10	7.8**	0.107–0.113	0.110	0.021	0.089	1.1

*After 53 hours at 30,000 r.p.m. and approximately 20°C.   ‡See table 2.
†After draining 10 minutes. Room temperature, 24°C.   **Estimated.

Analytical Centrifugation

Sediment obtained from the Mississippian crude oil was dispersed in normal heptane for a trial run in the Model E Spinco Ultracentrifuge. At low speeds of 20,000 to 40,000 r.p.m., no appreciable sedimentation could be observed within 10 to 15 minutes. Therefore, the speed of rotation was increased to the permissible maximum of 59,780 r.p.m., and after five to ten minutes a clarification of the solution became detectable at the meniscus.

Other preliminary centrifugation experiments were performed using petroleum ether as a solvent, and sedimentation was again observed. With both of these solvents, however, a considerable portion of the material rapidly sedimented to the bottom of the cell, indicating that the solvents were apparently causing an aggregation of the sediment and that it would be desirable to use a better dispersing agent.

Further analytical centrifugation experiments were carried out on the Mississippian sediment using benzene and carbon tetrachloride as solvents. These two solvents appeared satisfactory in that no dispersed sediment appeared to be aggregated. When benzene was used, it was noted that the Mississippian sediment was denser than the benzene, whereas, when carbon tetrachloride was used, the sediment floated (i.e., moved *toward* the center of rotation), indicating that its density was less than that of carbon tetrachloride. This suggested that further experimentation using these two solvents, and perhaps mixtures of the two to obtain intermediate solvent densities, would permit an accurate determination of the density of the sediment.

PREPARATIVE CENTRIFUGATION OF CRUDE OIL TO PRODUCE A SEDIMENTED FRACTION

Results with Illinois Crude Oils

To determine whether crude oil collected in air or in nitrogen would yield more sediment, a run was made on two samples of the Mississippian crude oil and the results are summarized in table 12.

On the basis of these data, it was concluded that the air-collected samples would be satisfactory to use for weight determinations of sediment. One might also infer that the colloidal-sized particles in the crude oil

TABLE 13.—COMPARISON OF SEDIMENT CENTRIFUGED FROM THREE ILLINOIS CRUDE OILS*

Crude oil	No. of tubes	Average oil per tube, gm.	Sediment plus oil film per tube†		Oil film, gm.‡	Average sediment per tube,	
			Range, gm.	Avg., gm.		gm.	% of oil
Pennsylvanian	10	7.64	0.043–0.074	0.054	0.023	0.031	0.4
Mississippian	9	7.85	0.099–0.114	0.108	0.021	0.087	1.1
Devonian	10	7.47	**		0.024	0.015††	0.2

*After 53 hours at 30,000 r.p.m. and approximately 20°C.
†After draining 10 minutes. Room temperature, 24° to 25°C.
‡See table 2.
**Some sediment present but was not packed firmly at bottom and appeared to be much less than was obtained with other two oils. Could not be weighed accurately because of excessive oil mixed with sediment.
††Estimated on the basis of subsequent four-day run on two tubes which gave 0.02 gm. and 0.04 gm. per tube.
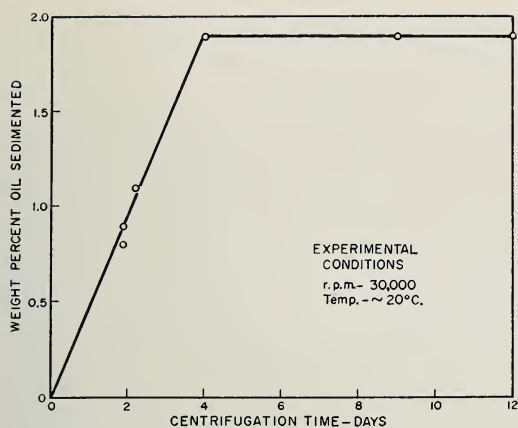
are not particularly affected by exposure to air encountered in the sampling and centrifuge techniques. To investigate this point further, both sediments were subjected to analytical centrifugation, discussed subsequently.

The amounts of sediment obtained from the three Illinois crude oils of different geologic age are summarized in table 13.

To obtain some idea of the total amount of sediment that could be centrifuged from the Mississippian crude oil, a number of experiments were made for various periods of time up to 12 days. The 12-day run actually was performed in three stages of 4, 5, and 3 days each. The results are summarized in table 14 and shown graphically on figure 8.

In the process of draining the centrifuged oils to evaluate the amounts of sediment obtained, a very thin film of material was sometimes observed to be packed along the length of the centrifuge tubes. This was observed with the Mississippian and Devonian oils but was not definitely established for the Pennsylvanian sample. These films could not feasibly be collected for testing and routine examination. They were gray, insoluble in benzene, and were tentatively identified as inorganic materials such as clays or salts. As will be discussed later, an attempt was made to obtain electron micrographs of the material.

Results with California Crude Oil

In preliminary investigations on the heavy, viscous, California crude oil, no indication of sediment was obtained after two days of preparative centrifugation at 30,000 r.p.m. Therefore, a more lengthy experiment was made wherein the California crude oil was centrifuged for a total of nine days at 30,000 r.p.m. After four days, two centrifuged tubes were removed from the rotor and divided into thirds by the previously described freezing technique. The corresponding fractions of each of the two tubes were combined and the five to six grams of sample in each fraction were diluted with approximately 100 ml. of normal pentane, or a pentane-oil weight ratio of about 12. The precipitate that formed was collected on filter paper, washed with additional normal pentane, dried, and

TABLE 14.—COMPARISON OF SEDIMENT CENTRIFUGED FROM MISSISSIPPIAN CRUDE
OIL OVER VARIOUS PERIODS OF TIME*

Days centrifuged	No. of tubes	Average oil per tube, gm.	Sediments plus oil film per tube†		Oil film, gm.‡	Average sediment per tube,	
			Range, gm.	Avg., gm.		gm.	% of oil
1.9	4	7.69	0.079–0.086	0.083	0.021	0.062	0.8
1.9	12	7.7**	0.081–0.096	0.088	0.021	0.067	0.9
2.2	9	7.85	0.099–0.114	0.108	0.021	0.087	1.1
4	2	7.59	0.156–0.173	0.165	0.021	0.144	1.9
9	2	7.51	0.162–0.168	0.165	0.021	0.144	1.9
12	4	7.63	0.162–0.170	0.165	0.021	0.144	1.9

*At 30,000 r.p.m. and approximately 20°C.
†After draining 10 minutes. Room temperature, 23° – 25°C.
‡See table 2.
**Estimated.

weighed. The same procedure was repeated with oil that had been centrifuged for nine days. The amounts of precipitate obtained in this manner are summarized in table 15.

TABLE 15.—PRECIPITATE FORMED IN MIXING NORMAL PENTANE WITH CALIFORNIA CRUDE OIL. FRACTIONS

Frac-tion*	Days centrifuged†	Weight gm.	Precipitate	
			gm.	% of oil
1	4	5.147	0.342	6.6
2	4	5.075	0.350	6.9
3	4	5.111	0.368	7.2
1	9	6.138	0.439	7.2
2	9	5.483	0.378	6.9
3	9	5.043	0.353	7.0

* 1 = top third, 2 = middle third, 3 = bottom third of frozen centrifuge tube.
†At 30,000 r.p.m. and approximately 20°C.

It will be noted that the amount of precipitate formed by this procedure is approximately 7 percent by weight for any of the fractions, regardless of the length of centrifugation. Using this same crude oil, Dunning et al. (1953) obtained an average of 10 percent pentane precipitate with essentially the same procedure.

The three fractions obtained after four days centrifugation were further investigated by measuring the interfacial tension of 0.1 weight percent solutions in benzene against water at 25°C. The interfacial tension measurements were made with a standard ring-type tensiometer and in accordance with the ASTM 971-50 procedure, which does not include aging effects. The results of these measurements are summarized in table 16, and it will be seen that the differences in the interfacial tensions of the three fractions do not suggest the progressive change in interfacial activity from the top to the bottom of the tube that might be anticipated if separation of heavy asphaltic particles had occurred.

Although there was no positive indication that centrifugal separation of asphaltic materials had occurred in the California crude oil, it was noted that a light gray-white film of very finely divided particles collected along the length of each centrifuge tube. Substantially more of this material was collected in centrifuging the California crude oil than was collected in the work on Illinois crude oils. Therefore, several centrifuge tubes of the California crude oil were allowed to drain for about a day, and the tubes were washed with benzene to remove the remaining oil film. The grayish-white, apparently inorganic sediment was then prepared for electron microscopy investigations, to be discussed later. The amount of this sediment was very small; one tube contained approximately four milligrams, or about 0.05 percent of the oil by weight.

ANALYTICAL CENTRIFUGATION TO CHARACTERIZE CRUDE OIL SEDIMENT

Experimental Data

Sediments that had been separated from crude oil were dispersed in benzene, carbon tetrachloride, and mixtures of the two, and then examined in the analytical ultracentrifuge. On the basis of the preliminary investigations, runs were carried out at 60,000 r.p.m., and exposures were made of the sedimentation boundaries at intervals of 8, 16, or 32 minutes, depending on the rate of boundary movement. Five, and occasionally ten, photographs were made for each run. The photographs for two typical runs are shown in plate 1. The numbers from top to bottom give the sequence of exposures. Run No. A-1867 shows

TABLE 16.—INTERFACIAL TENSIONS OF 0.1 WEIGHT PERCENT SOLUTIONS OF CALIFORNIA CRUDE OIL FRACTIONS IN BENZENE AGAINST WATER AT 25°C.

Fraction*	Interfacial tension, dynes/cm.
Benzene†	33.2
1	28.2
2	29.0
3	28.3

*1 = top third, 2 = middle third, 3 = bottom third of frozen centrifuge tube.
†Benzene against water for reference purposes.

TABLE 17.—LIGHT TRANSMISSION READINGS ON NEGATIVES OF RUN NO. A-1867 FOR MISSISSIPPIAN SEDIMENT DISPERSED IN BENZENE*

Exp.	Turns of Wheel on Densitometer Mechanical Drive†																	PM‡	TT**
	10	20	30	40	50	60	70	80	90	100	110	120	130	135	140	145	150		
1	86.5	84.8	74.5	85.2	88.3	91.0	80.2	59.2	57.0	71.4	74.2	80.8	74.1	72.0	57.3	32.8	6.8	152.0	172.2
2	92.9	86.5	93.0	89.3	89.8	87.8	88.7	84.0	77.7	80.2	78.7	68.7	43.7	—	11.8	—	2.6	152.0	172.1
3	95.3	92.0	93.8	93.3	95.3	97.1	103.0	97.3	88.7	81.8	59.6	36.7	14.3	—	4.0	—	1.7	152.0	172.4
4	98.8	93.3	85.7	89.2	91.5	92.2	87.3	75.8	66.8	48.5	31.2	17.0	7.0	—	2.6	—	1.5	152.0	172.5
5	93.3	89.3	89.7	86.0	82.5	81.9	67.0	56.5	42.9	32.7	17.7	8.5	4.1	—	1.5	—	0.9	152.0	172.0
Average																		152.0	172.2

*Refer to print of this negative in plate 1.
†Number of turns starting from right reference line and moving toward left reference line.
‡Position of meniscus, turns from right reference line.
**Total turns from right to left reference lines.

sedimentation in benzene wherein the boundary moved from left to right (in the direction of the centrifugal field). Run No. A-1783 shows flotation in carbon tetrachloride wherein the boundary moved from right to left (counter to the direction of the centrifugal field).

As has been explained, in these light-absorption photographs the point of 50 percent light transmission may be taken as the sedimentation boundary. Therefore, its position on each photograph was determined by scanning the film negative from the right reference (RR) to the left reference (LR), using the Spec-Reader densitometer. An example of typical data is shown in table 17 for run No. A-1867. As indicated, light-transmission readings were taken at a certain number of turns of the mechanical drive that moved the film negative past the fixed light source of the densitometer. The number of turns shown start with zero at RR and increase to the total turns required to reach LR. The turns to the position of the meniscus and to the bottom of the cell (determined only when flotation occurred) also were recorded. In taking these data, all five exposures were scanned along a line parallel to the edge and at the same position on each exposure. The position of this line was selected at what was judged to be average conditions, and, by making readings along a fixed line, variations in light intensity across the width of the cell were minimized.

The light-transmission readings of table 17 are plotted on figure 10 for run No. A-1867 to illustrate the general nature of the data for sedimentation. Readings obtained on the film negatives of run No. A-1783 are plotted on figure 11 to illustrate typical data for flotation. For the most part the plotted points follow smooth curves from 0 up to 80 or 90 percent, after which deviations occur which were more a function of film emulsion grain size and developing procedures than anything else. In the areas of high percentage light transmission, estimates of the maximum average value were made to the nearest percent as indicated. The curves were not completed
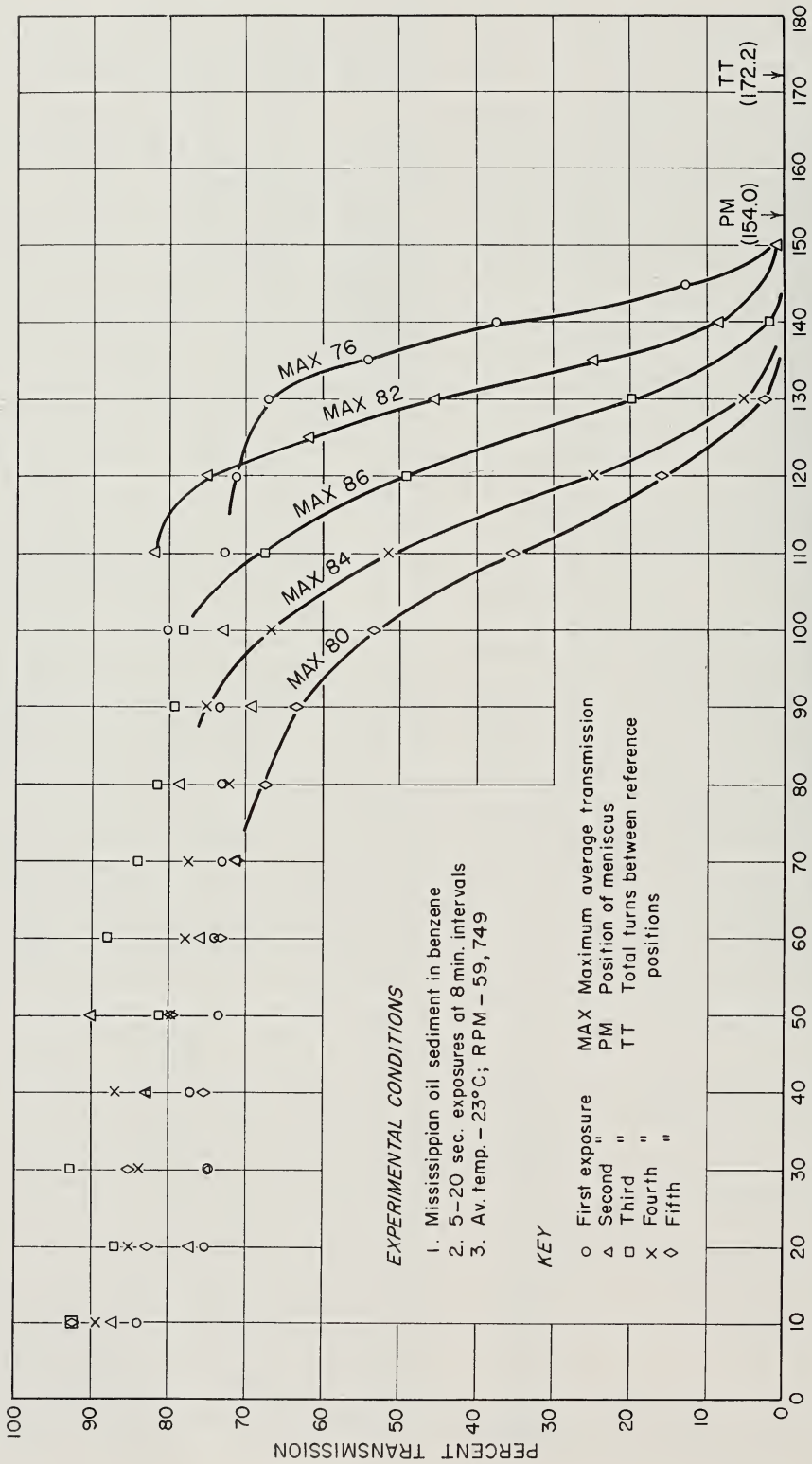
FIG. 9.—Light transmission readings from negative of run No. A-1778.

TABLE 18.—SUMMARY OF ANALYTICAL CENTRIFUGATION EXPERIMENTS

Fig. no.	Crude oil	Collected under	Sediment dispersed in*	Average conditions		Run no.†
				°C	RPM	
9	Mississippian	Nitrogen	B	23.0	59,749	A–1778
10	Mississippian	Nitrogen	B	23.9	59,700	A–1867
11	Mississippian	Nitrogen	C	24.3	59,731	A–1783
12	Mississippian	Nitrogen	⅔B+⅓C	24‡	59,774	A–1898
13	Mississippian	Nitrogen	⅓B+⅔C	25.6	59,750**	A–1851
14	Mississippian	Air	B	22.4	59,798	A–1782
15	Mississippian	Air	B	23.6	59,740	A–1869
16	Mississippian	Air	C	23.0	59,750**	A–1798
17	Pennsylvanian	Air	B	23.0	59,743	A–1877
18	Devonian	Nitrogen	B	23‡	59,737	A–1892
19	n-Heptane-Miss.††	Air	B	23.0	59,768	A–1878
20	Benzene-Miss.††	Air	B	23.4	59,728	A–1879

*B is benzene, C is carbon tetrachloride.
†File numbers assigned to film negatives and data sheets in Ultracentrifuge Laboratory, University of Illinois.
‡Approximate temperature.
**Assumed average value as speed control setting was same for all runs.
††1:1 mixture with crude oil by volume.

because of the confusing array of lines that would result, but all points are shown that do not overlap much. Occasional points above 100 percent were omitted.

A number of analytical centrifugation runs were made on this Mississippian sediment, and one run also was made on sediment obtained from each of the Devonian and Pennsylvanian crude oils. In addition, one run was made on sediment centrifuged from a 1:1 mixture (by volume) of nor-

mal heptane and Mississippian crude oil. A 1:1 mixture of benzene and this oil yielded a very limited amount of sediment that was not clearly separated from the supernatant liquid and this also was examined. A summary of the experimental conditions is given on table 18. The light-transmission readings are plotted in figures 9 through 20 and these figure numbers are included on table 18 for reference purposes.
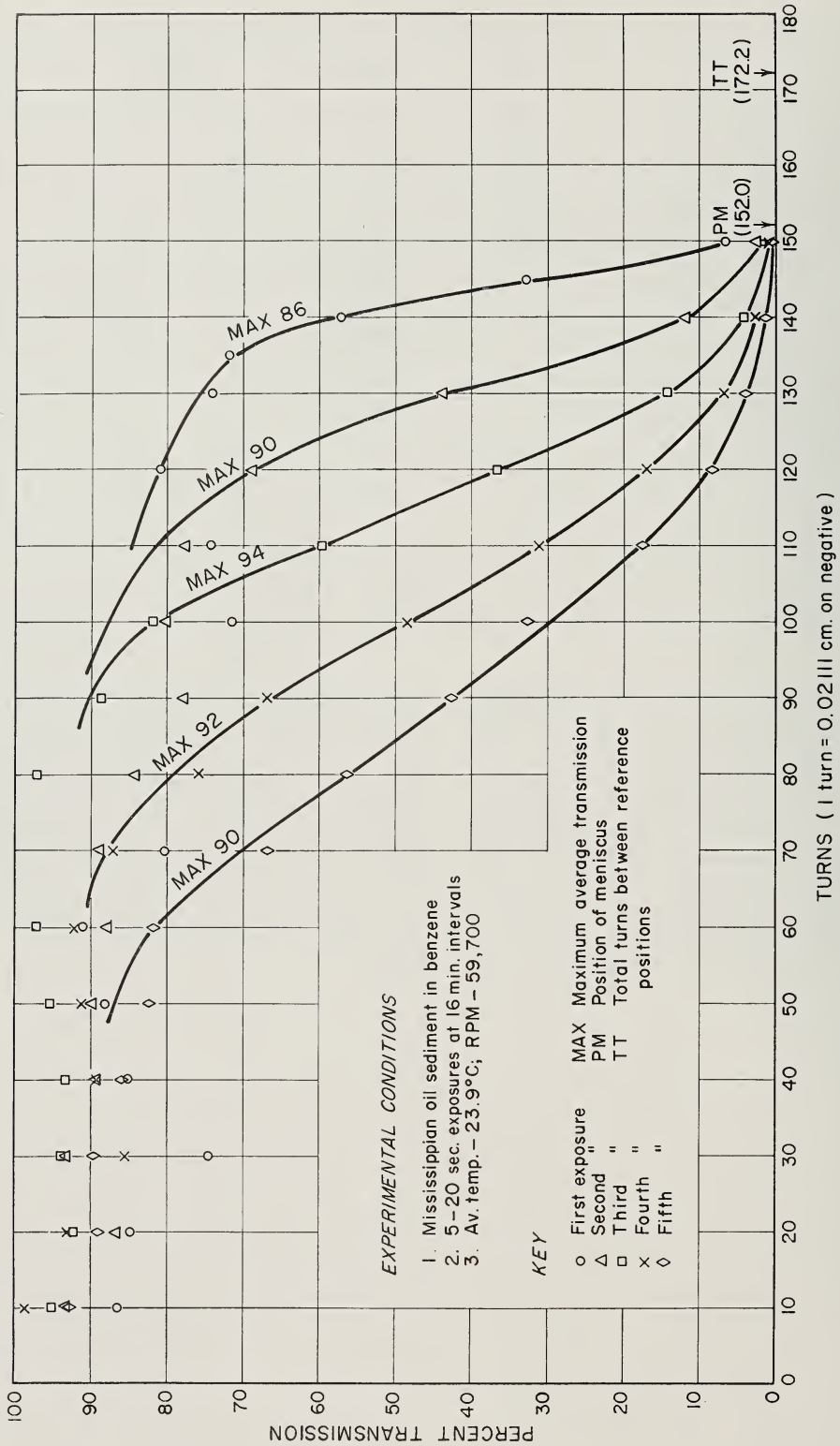
Fig. 10.—Light transmission readings from negative of run No. A-1867.
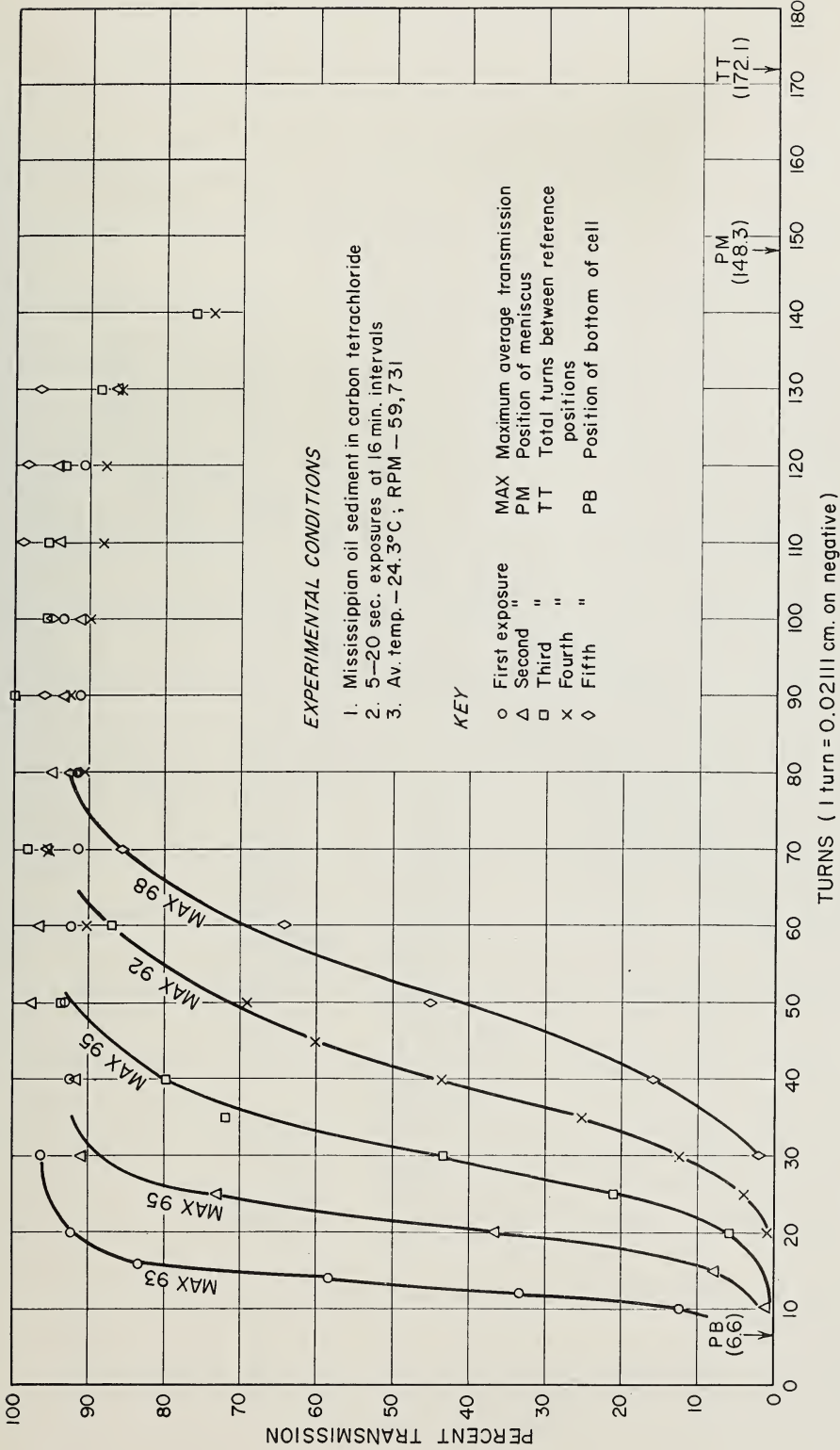
Fig. 11.—Light transmission readings from negative of run No. A-1783.
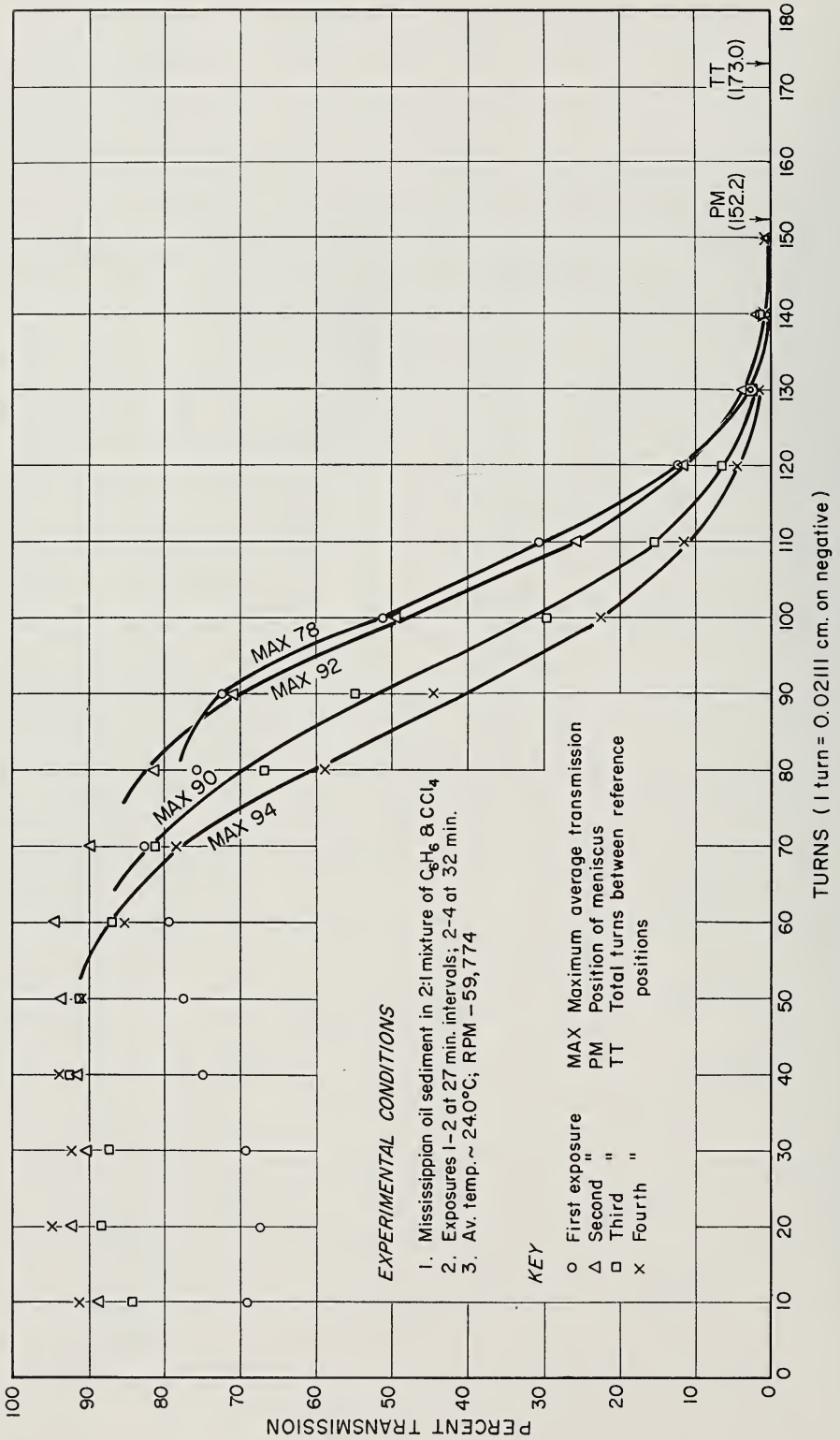
Fig. 12.—Light transmission readings from negative of run No. A-1898.
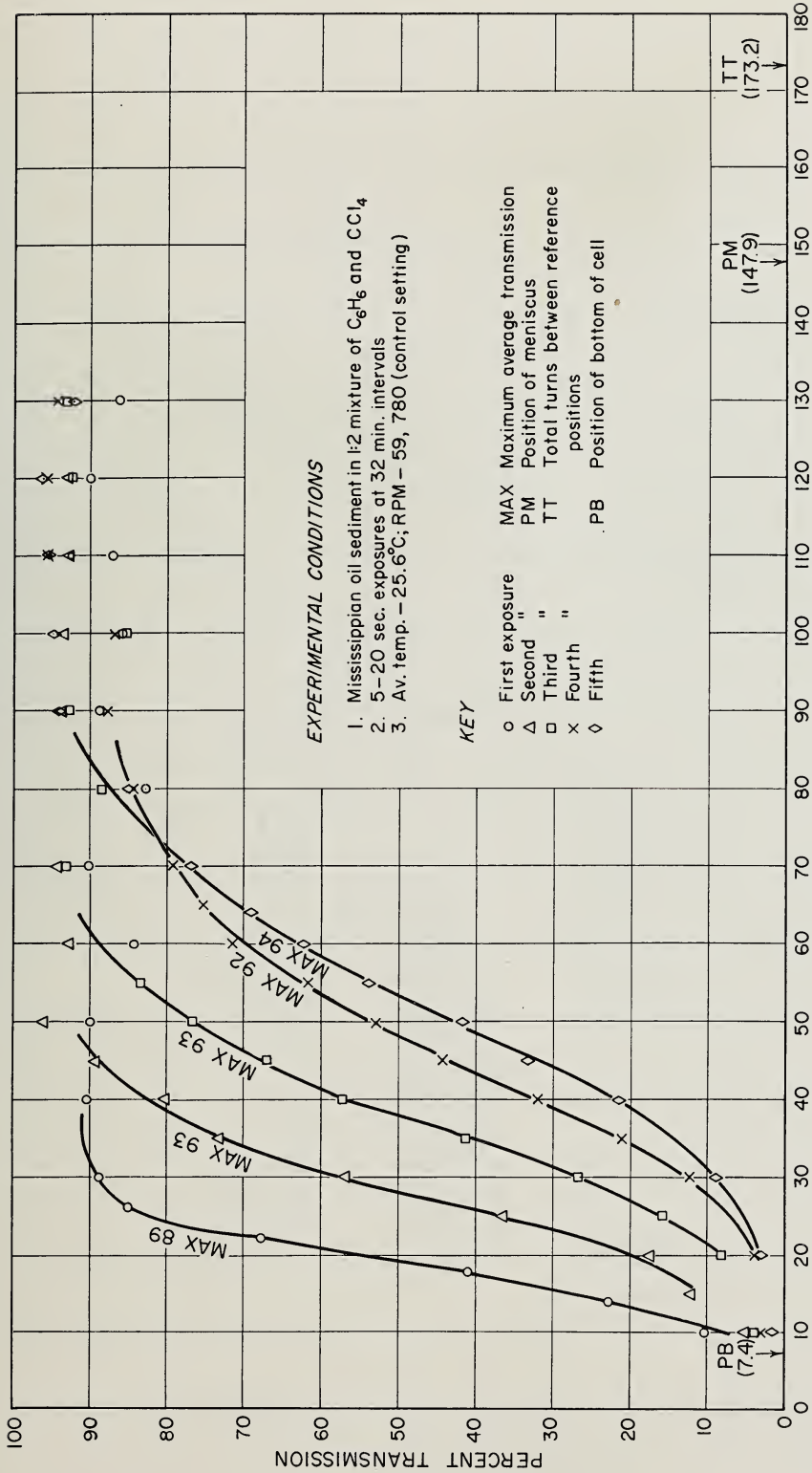
Fig. 13.—Light transmission readings from negative of run No. A-1851.
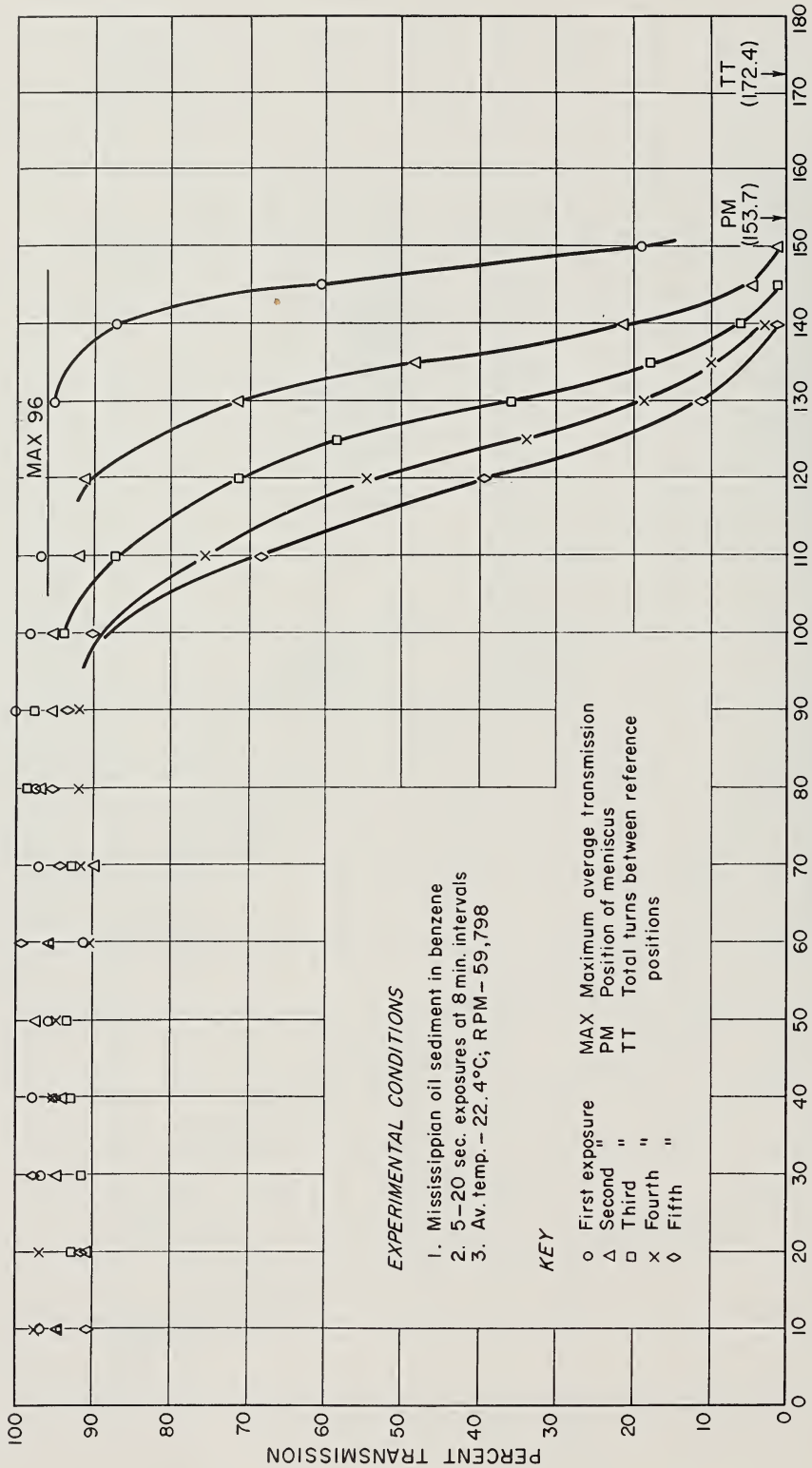
Fig. 14.—Light transmission readings from negative of run No. A-1782.
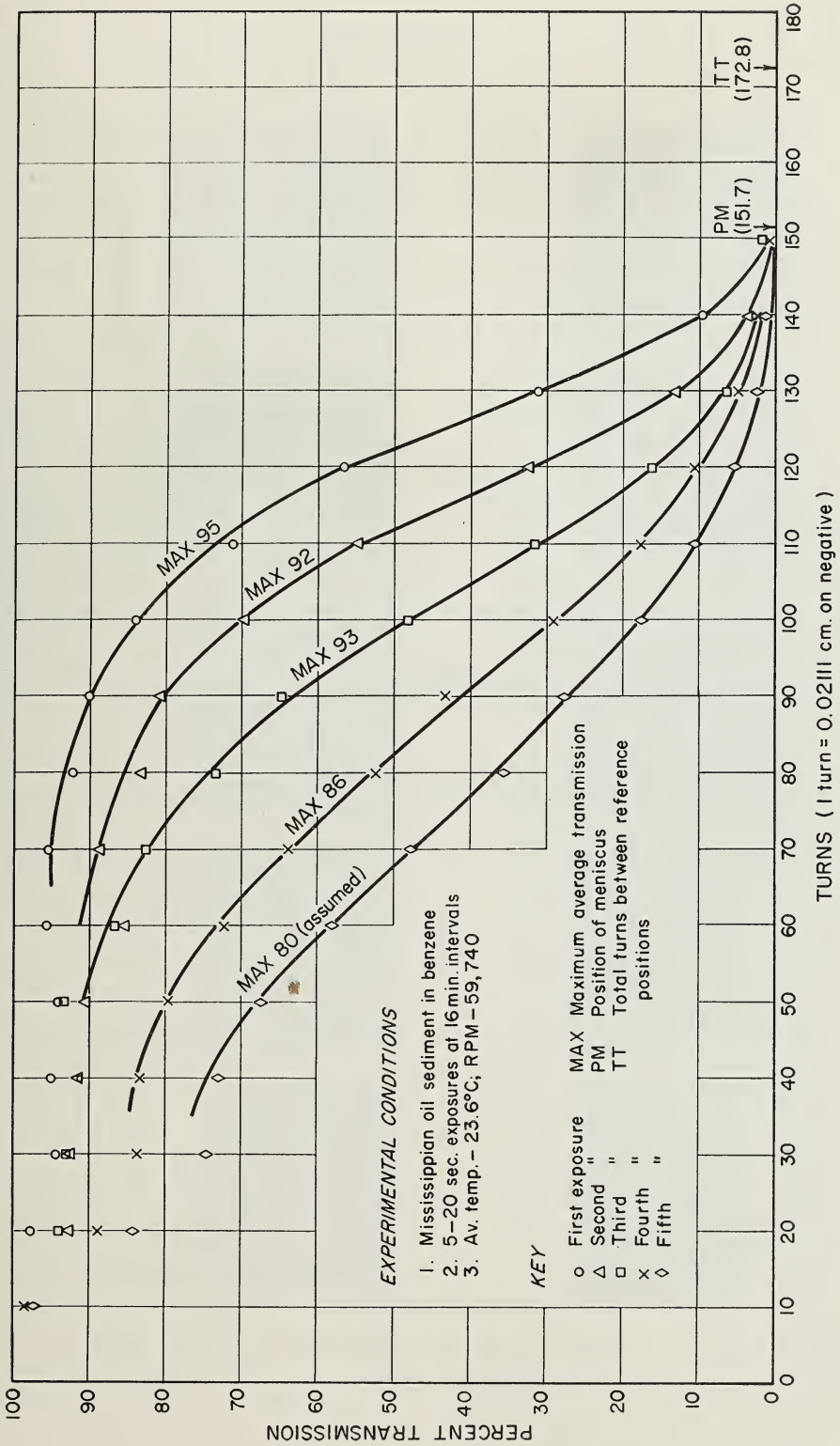
FIG. 15.—Light transmission readings from negative of run No. A-1869.

EXPLANATION OF PLATE 1

Typical results obtained in analytical centrifugation, sediment from Mississippian crude oil dispersed in benzene and in carbon tetrachloride.

Experimental conditions:

Run No. A-1867 (dispersed in benzene): r.p.m.—59,700; av. temp.—23.9°C.; five 20-second exposures at 16-minute intervals.

Run No. A-1783 (dispersed in carbon tetrachloride): r.p.m.—59,731; av. temp. 24.3°C.; five 20-second exposures at 16-minute intervals.

Explanation: LR—left reference
PM—position of meniscus
SB—approximate position of sedimentation boundary
PB—position of bottom of cell
RR—right reference

Run No. A-1867   Run No. A-1783

LR PM SB   RR   LR PM   SB PB RR
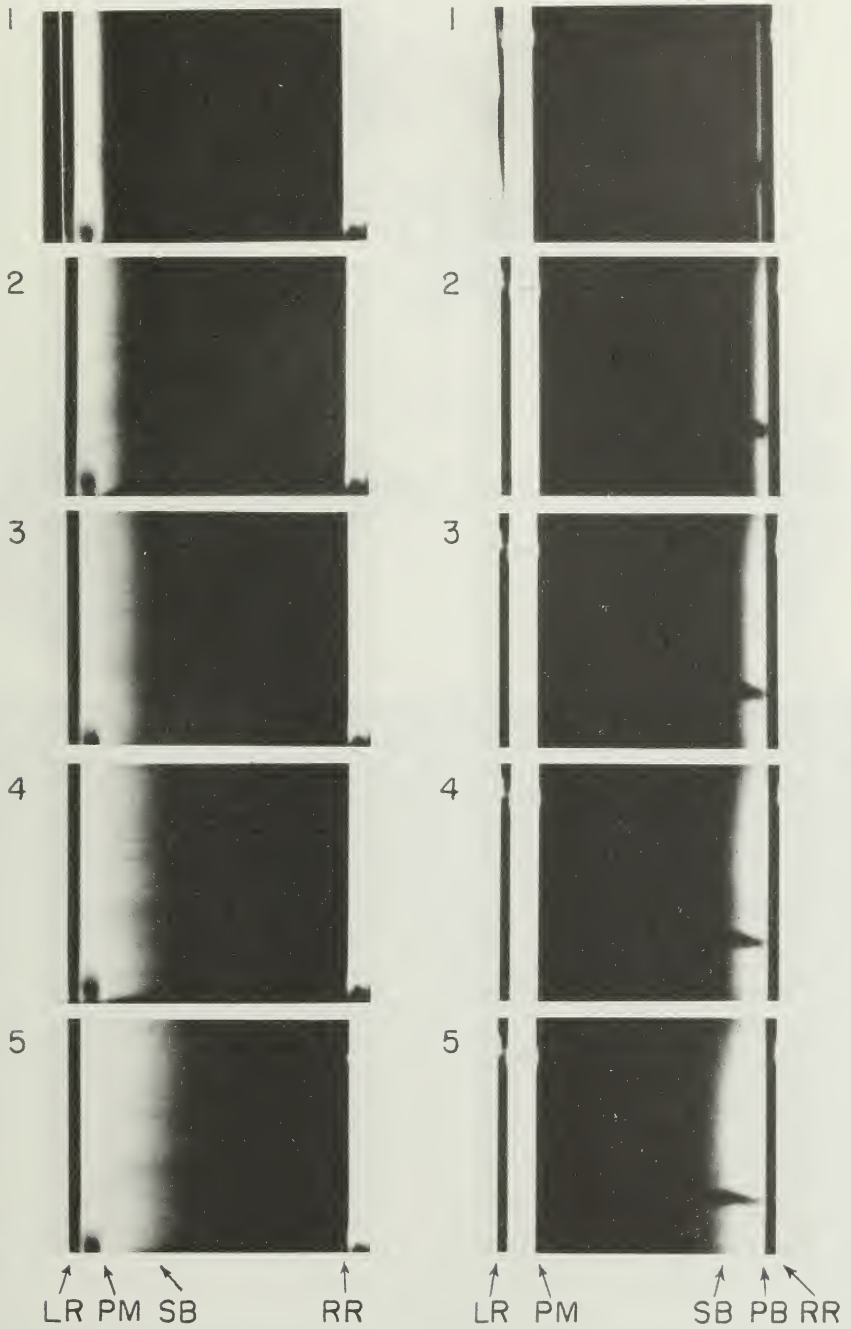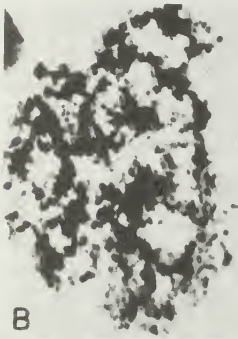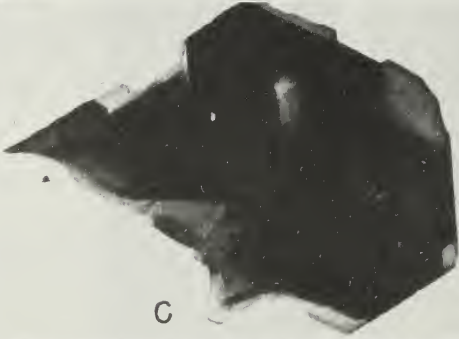
EXPLANATION OF PLATE 2

Electron micrographs of sediment centrifuged from Mississippian crude oil:

    A.—X 33,000; B.—X 18,000; C.—X 35,000.

D.—Electron micrograph of muscovite surface on which crude oil sediment was prepared, X 100,000. Pseudo-replica obtained by platinum shadow backed up with carbon film.

E.—Electron micrograph of sediment centrifuged from crude oil, X 100,000. Pseudo-replica obtained by platinum shadow backed up with carbon film.
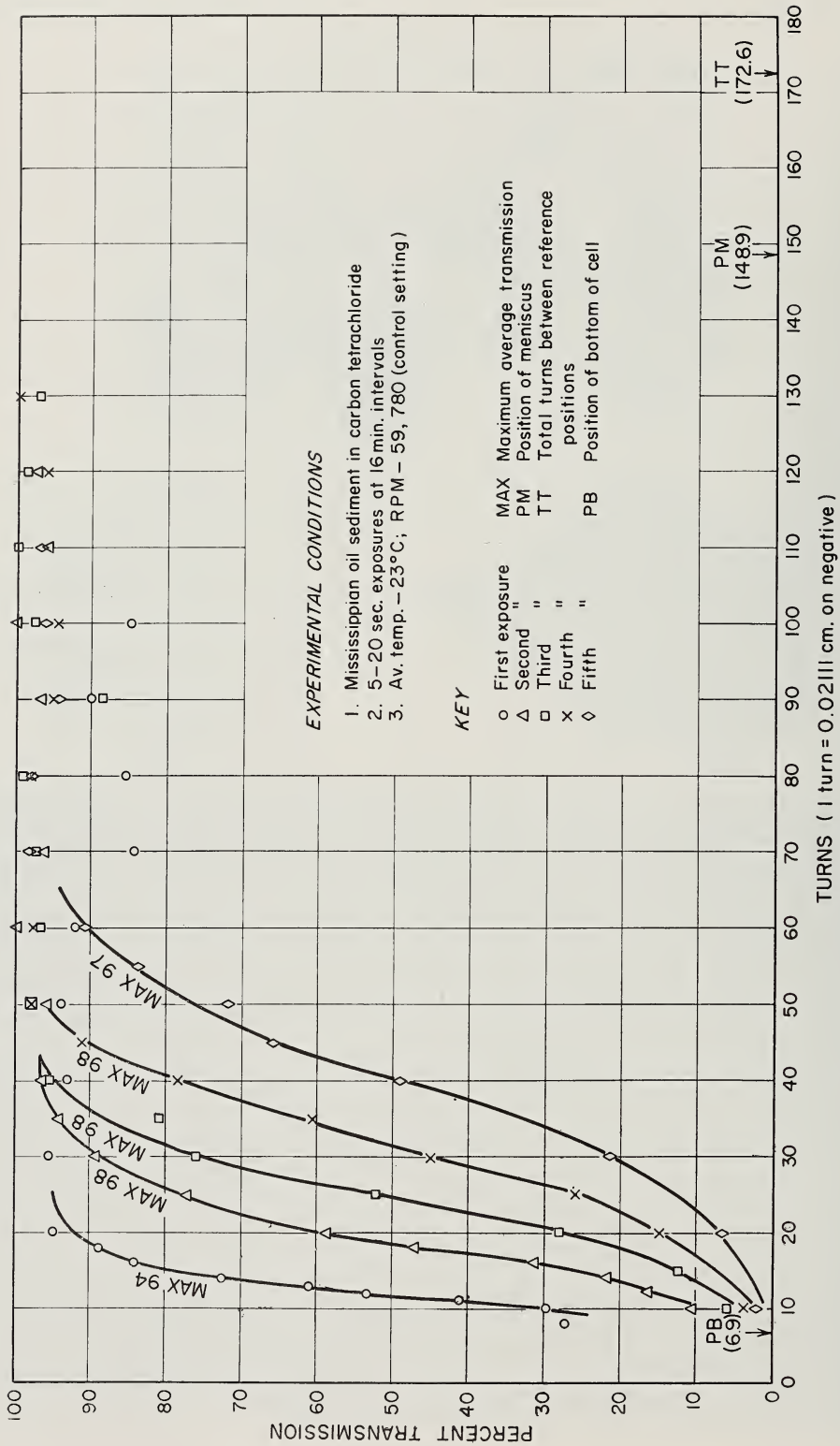
Fig. 16.—Light transmission readings from negative of run No. A-1798.

EXPERIMENTAL CONDITIONS

1. Mississippian oil sediment in carbon tetrachloride
2. 5–20 sec. exposures at 16 min. intervals
3. Av. temp.–23°C; RPM–59,780 (control setting)

KEY

o	First exposure	MAX	Maximum average transmission
△	Second "	PM	Position of meniscus
□	Third "	TT	Total turns between reference positions
×	Fourth "		
◇	Fifth "	PB	Position of bottom of cell
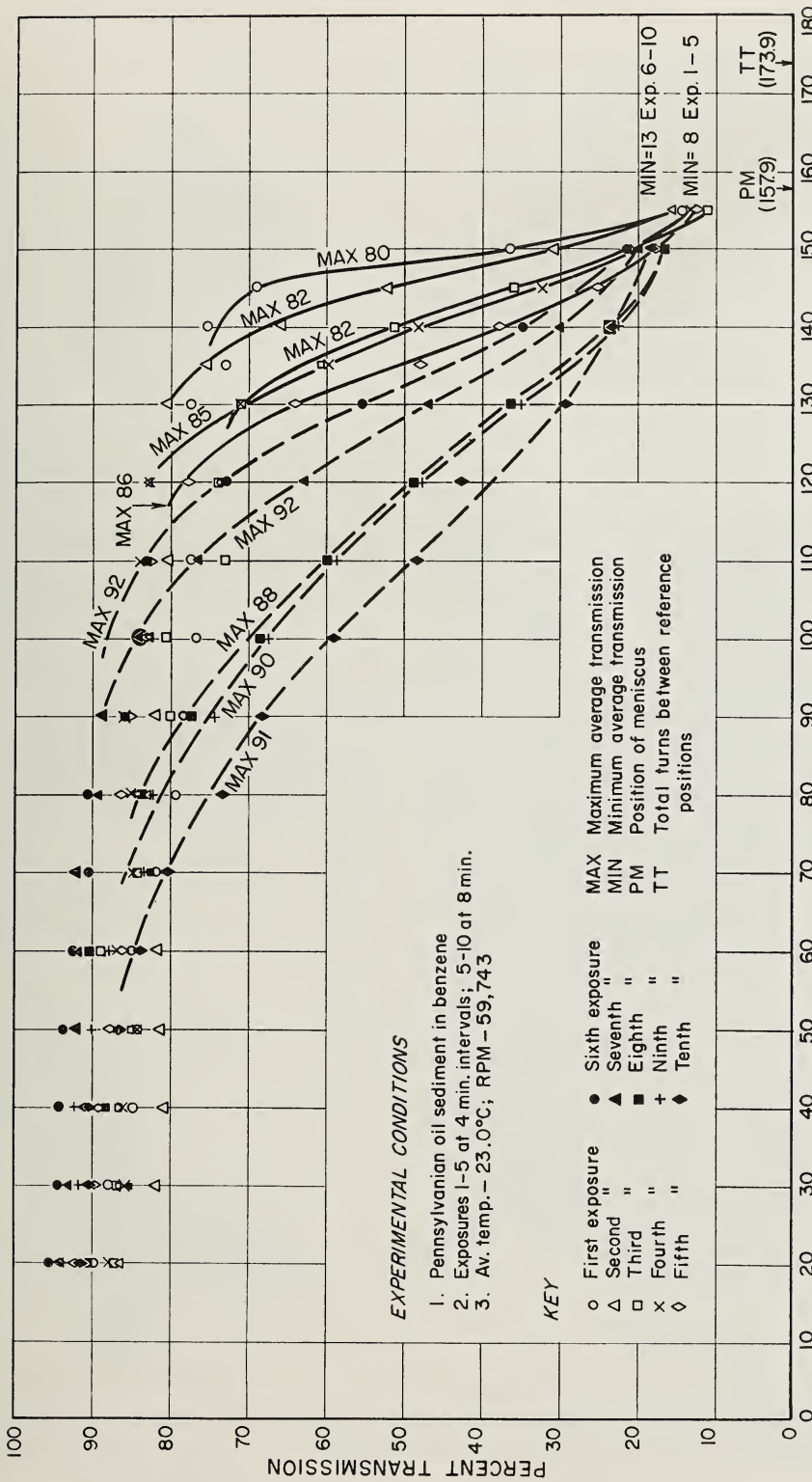
FIG. 17.—Light transmission readings from negative of run No. A-1877.

EXPLANATION OF PLATE 3

Electron micrographs of inorganic sediment centrifuged from Mississippian (A and B), Devonian (C and D), and California (E and F) crude oils. Pseudo-replicas obtained by chromium shadow backed up with carbon film.

Mississippian: A.—X 40,000; B.—X 32,000

Devonian: C.—X 26,000; D.—X 18,000

California: E.—X 45,000; F.—42,000

WITHERSPOON—STUDIES ON PETROLEUM WITH THE ULTRACENTRIFUGE
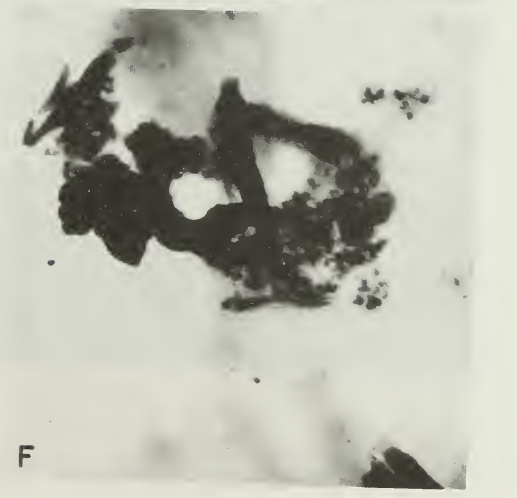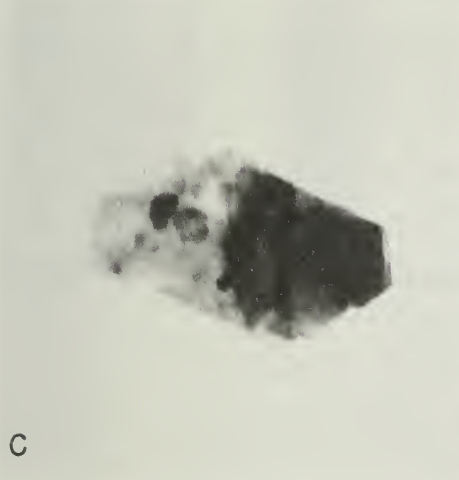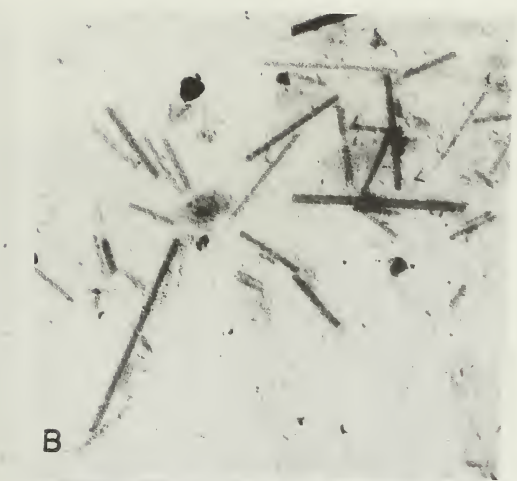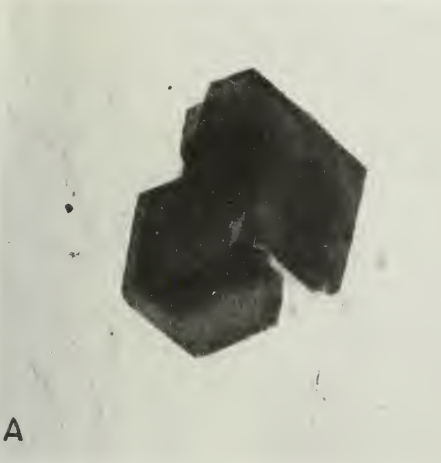
A.—Centrifugal fractionation of Mississippian crude oil after 12 days at 30,000 r.p.m. and 20°C.
Tube on left contains uncentrifuged oil and tube on right contains centrifuged oil. Both tubes illuminated from same source of transmitted and reflected light.

B.—Three fractions separated from Mississippian crude oil after 12 days centrifugation at 30,000 r.p.m. and 20°C.

From left to right: uncentrifuged oil; top fraction, middle fraction, and bottom fraction of centrifuged oil shown in A.

C.—Color banding in Heptane-Mississippian crude oil mixtures after 58 hours at 30,000 r.p.m. in angle head rotor.

Tube on left contains 1:1 mixture; tube on right contains 2:1 mixture.

D.—Color banding in Heptane-Mississippian crude oil mixtures after 60 hours at 28,000 r.p.m. in swinging bucket rotor.

Tube on left contains 1:1 mixture; tube on right contains 2:1 mixture.
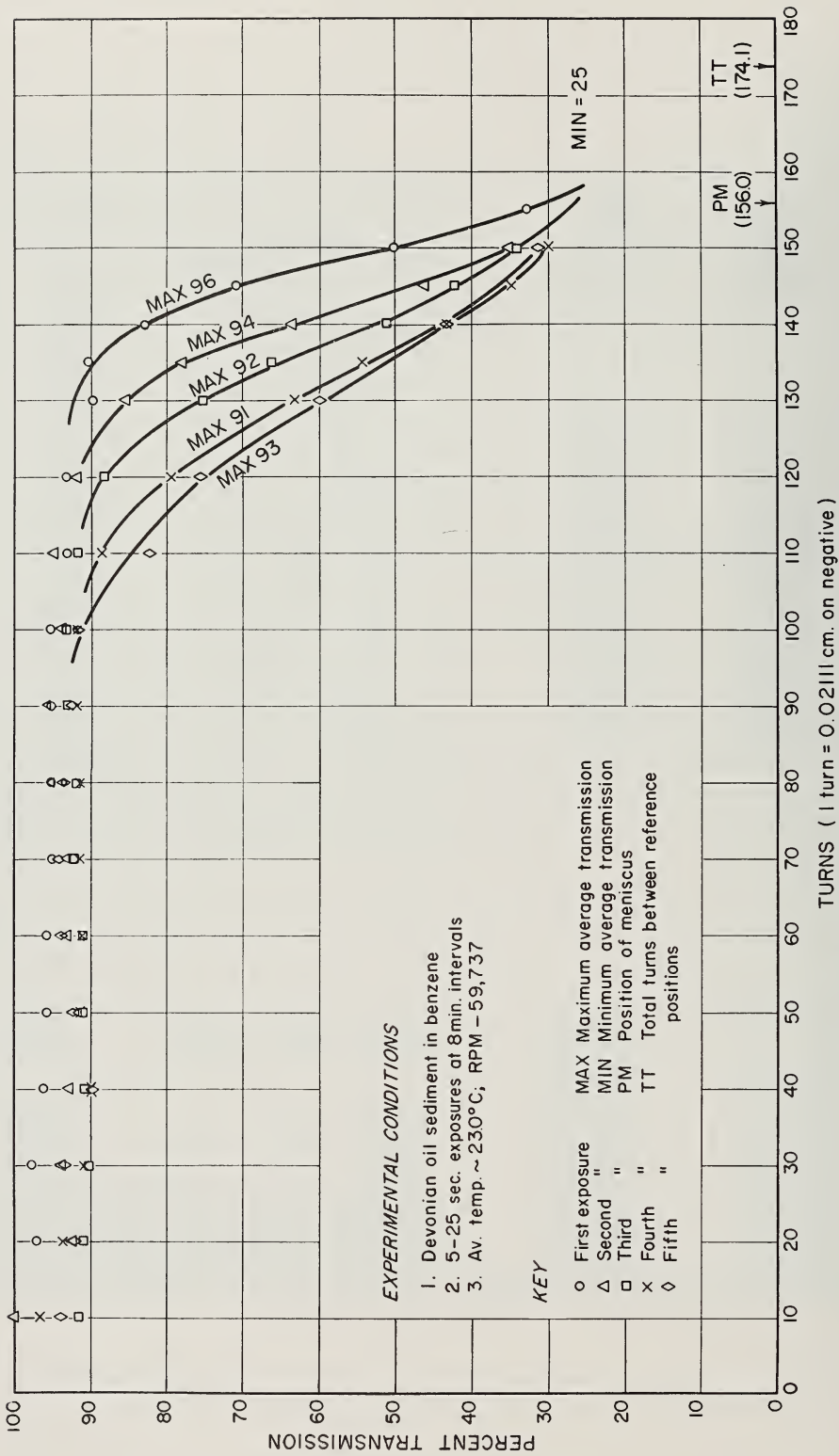
Fig. 18.—Light transmission readings from negative of run No. A-1892.
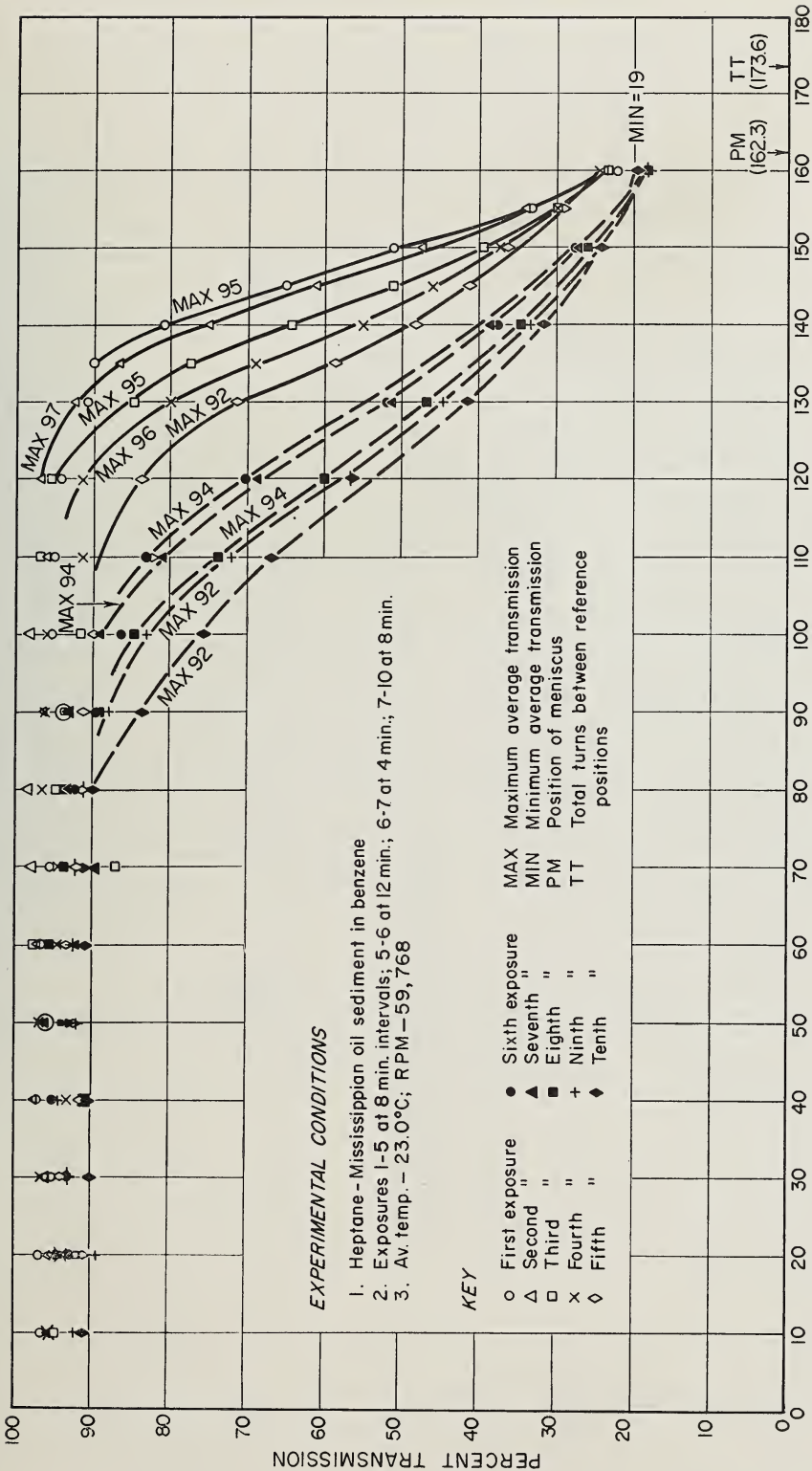
Fig. 19.—Light transmission readings from negative of run No. A-1878.
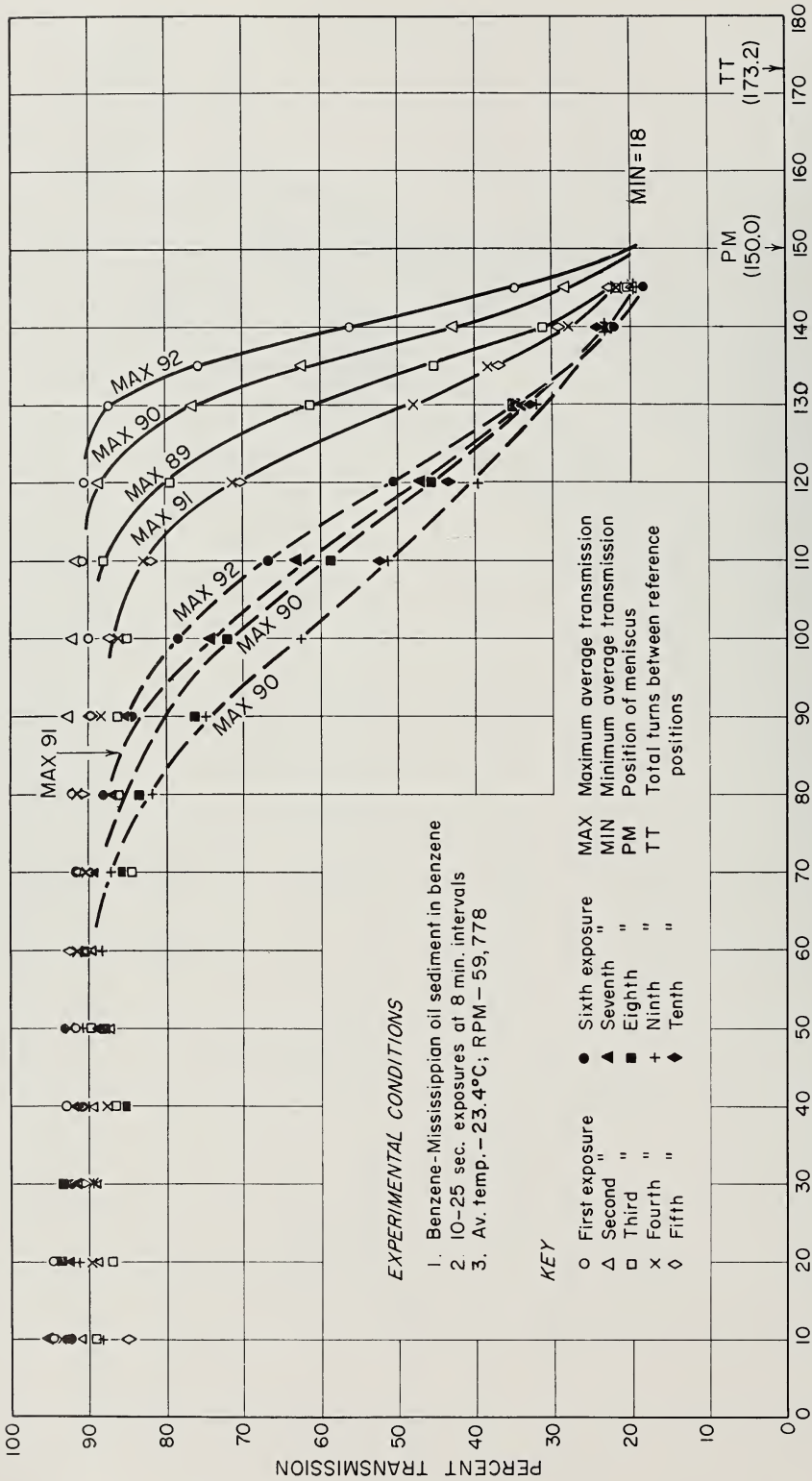
FIG. 20.—Light transmission readings from negative of run No. A-1879.

Sedimentation Coefficients and Particle Densities

The light transmission curves provide the basic data for calculating sedimentation coefficients from which particle size and molecular weight may be computed. The following discussion of the curves on figure 10 will illustrate the method employed.

The curves exhibit a decreasing slope with each succeeding exposure, that is, the boundaries become more diffuse with time. Two effects are responsible. One is diffusion taking place across the concentration gradient. In addition, if there is an appreciable range in the size of the sedimenting particles, the larger particles will move faster than the smaller ones. Thus the sedimentation boundary, which starts as a relatively sharp line, gradually becomes more diffuse. The position of the 50 percent light transmission on each curve is, to a sufficient approximation, the middle of the boundary, or the position that the boundary would have in the absence of diffusion and heterogeneity. Positions of the boundary were therefore obtained from each individual curve by recording the number of turns equal to a light-transmission reading that was half the difference between the maximum and minimum values. Minimum readings were usually zero; when other than zero, they are indicated on the graphs.

The position of the boundary as measured in turns of the mechanical drive was converted to its equivalent position in the cell. Calibration of the mechanical drive on the densitometer indicated 1 turn to be equivalent to 0.02111 cm. on the film negative, and by virtue of the magnification in the optical system of the ultracentrifuge, distances on the negative are 2.315 times the true distance in the centrifuge cell. The ultracentrifuge rotor is machined so that the midpoint between the reference lines, LR and RR, is 6.500±0.006 cm. from the center of rotation. With this information, the absolute distances of the meniscus, sedimentation boundary, and bottom of the cell could now be calculated. As discussed previously, these dimensions are necessary for determining rate of sedimentation and calculating correction factors for compressibility effects.

It may be of interest to indicate the precision with which distances could be determined in the cell. No difficulty was encountered in measuring end positions on the negatives to 0.1 turn of the densitometer wheel, and the positions of the sedimentation boundaries were reproducible to ± 1 turn. As distances are of the order of 6.0 cm. or greater, the uncertainty in the boundary should not exceed 0.25 percent.

TABLE 19.—SEDIMENTATION BOUNDARY DATA FROM RUN NO. A–1867 FOR MISSISSIPPIAN SEDIMENT DISPERSED IN BENZENE*

| Exp. | Time, min. | RR to SB, turns | Midpoint on photograph to SB | | Center of rotation to SB | | Distance from meniscus, cm. | F†† | log x_c‡‡ |
			turns†	cm.‡	cm.**	log x			
1	0	143.0	56.9	0.52	5.98	0.7767	0.08	1.00005	0.7767
2	16	129.6	43.5	0.40	6.10	0.7853	0.20	1.00038	0.7856
3	32	115.3	29.2	0.27	6.23	0.7945	0.33	1.00104	0.7953
4	48	101.3	15.2	0.14	6.36	0.8035	0.46	1.00196	0.8051
5	64	88.4	2.3	0.02	6.48	0.8116	0.58	1.00307	0.8141
PM		152.0	65.9	0.60					
LR		172.2							

*RR = right reference, SB = position of sedimentation boundary, PM = position of meniscus, LR = left reference.
†172.2/2 = 86.1. For exposure 1, 143.0 −86.1 = 56.9 turns.
‡Turns times 0.02111 divided by 2.315.
**For exposure 1, 6.50 − 0.52 = 5.98 cm.
††Correction factors from figure 5.
‡‡F · log x = log x_c (corrected for compressibility).
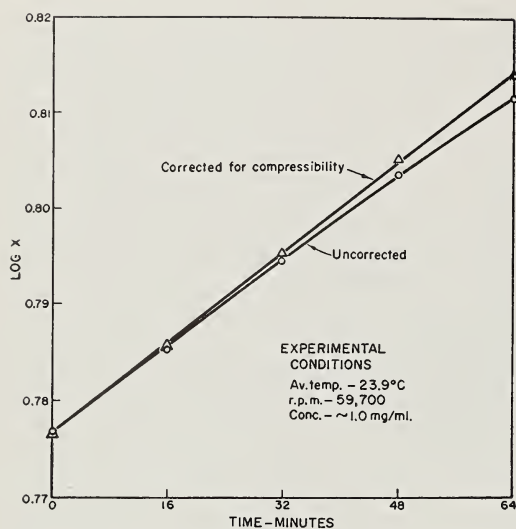
Fig. 21.—Log x versus time for run No. A-1867.

An example of the way in which the experimental data were analyzed is summarized in table 19 for run No. A-1867.

The plot of log x versus time from table 19, which is shown in figure 21, will give an idea of the rate of sedimentation in benzene. It will be noted that the points for the lower line, before any corrections are made for compressibility, appear to lie

on a slight curve. The amount of curvature shown is to be expected from theoretical considerations (fig. 3). Ordinarily, however, the spread in the data of other runs was such that curvatures of this low magnitude could not be detected with certainty.

It is customary to calculate the sedimentation coefficient by dividing the slope of a plot of ln x (or 2.303 log x), versus t by the square of the angular velocity, w^2. Therefore, the best straight line was drawn through the uncorrected experimental data on figure 21, and the slope was calculated to be $5.56 \cdot 10^{-4}$ min.$^{-1}$. As run No. A-1867 was made at 59,700 r.p.m. the sedimentation coefficient, s, is:

$$s = \frac{2.303 \, (5.56 \cdot 10^{-4})}{\left(\frac{2 \, \pi \, 59{,}700}{60}\right)^2 60} = 5.46 \cdot 10^{-13} \text{ sec.}$$

Sedimentation coefficients were calculated from the uncorrected experimental data in this manner and are summarized in the fifth column of table 20. As the analytical centrifugation runs shown in figures 9 through 13 were all for portions of the same sediment dispersed in media of four differ-

Table 20.—Experimental Sedimentation Coefficients Corrected for Compressibility

Fig. no.	Crude oil	Collected under	Sediment dispersed in*	Sed. coefficients		Percent change in s
				uncorr. s x 10¹³, sec.	corr. s_c x 10¹³, sec.	
9	Mississippian	Nitrogen	B	7.02	7.40	5.4
10	Mississippian	Nitrogen	B	5.46	5.73	4.9
11	Mississippian	Nitrogen	C	−3.19	−4.15	30.1
12	Mississippian	Nitrogen	⅔B+⅓C	1.25	1.57	25.6
13	Mississippian	Nitrogen	⅓B+⅔C	−1.62	−1.57	−3.1
14	Mississippian	Air	B	5.38	5.58	3.7
15	Mississippian	Air	B	4.41	4.84	9.8
16	Mississippian	Air	C	−2.36	−3.00	27.1
17	Pennsylvanian	Air	B	4.70	4.99	6.2
18	Devonian	Nitrogen	B	3.92	4.10	4.6
19	n-Heptane-Miss.	Air	B	2.75	2.92	6.2
20	Benzene-Miss.	Air	B	3.45	3.59	4.1

*B is benzene, C is carbon tetrachloride.
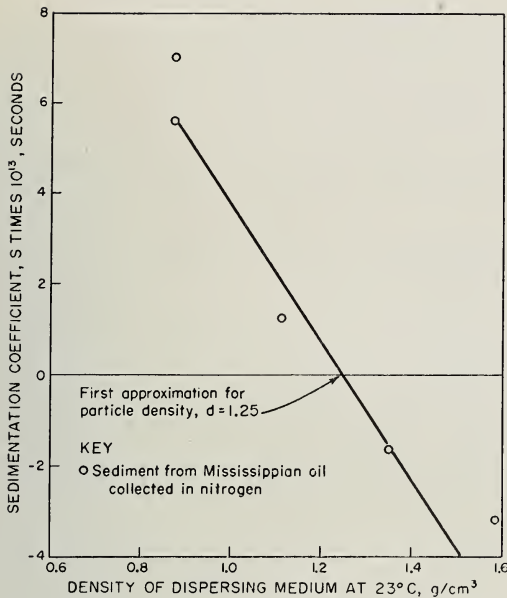
FIG. 22.—Uncorrected sedimentation coefficients versus density of dispersing medium. Mississippian oil sediment dispersed in benzene.

ent densities, it was possible to make a rough estimate of the effective density of the dispersed particles by plotting the uncorrected coefficients versus densities. As indicated in figure 22, the particles would have a zero sedimentation coefficient if dispersed in a liquid of 1.25 g/cm.³ density. Therefore, this value was adopted as a first approximation for the particle density and subsequently was used in computing the correction factors for compressibility effects.

An example of the correction factors due to benzene compressibility is included in table 19 and the corrected values of log x_c are plotted on figure 21. Although the correction factors listed in table 19 appear to be quite small, numerically the net increase in slope is appreciable, 4.9 percent for this benzene solution. All sedimentation coefficients were corrected for compressibility, and the corrected coefficients, s_c, for each run are included in table 20. It will be noted that the effect of compressibility can amount to 30 percent depending on the dispersion medium.

The corrections for compressibility in effect relate the experimental data to conditions of sedimentation at the menisci of the various dispersing agents used. However, the viscosities of the four different media are not the same, and it is necessary to correct the sedimentation coefficients to some standard reference viscosity. The viscosity

TABLE 21.—SEDIMENTATION COEFFICIENTS CORRECTED TO VISCOSITY OF BENZENE
AT 23°C. AND 1 ATMOSPHERE*

Fig. no.	Dispersing medium				Corr. factor‡	Sed. coefficients	
	comp.†	temp. °C.	density g/cm.³	viscosity cp.		uncorr. $s_c \times 10^{13}$ sec.	$(s°)_c \times 10^{13}$ sec.
9	B	23.0	0.8752	0.622	1.0000	7.40	7.40
10	B	23.9	0.8741	0.611	0.9796	5.73	5.61
11	C	24.3	1.5857	0.911	1.4756	−4.15	−6.12
12	⅔B+⅓C	24**	1.1129	0.695	1.1124	1.57	1.75
13	⅓B+⅔C	25.6	1.3470	0.777	1.3008	−1.57	−2.04
14	B	22.4	0.8758	0.625	1.0064	5.58	5.62
15	B	23.6	0.8745	0.614	0.9850	4.84	4.77
16	C	23.0	1.5882	0.928	1.4920	−3.00	−4.48
17	B	23.0	0.8752	0.622	1.0000	4.99	4.99
18	B	23**	0.8752	0.622	1.0000	4.10	4.10
19	B	23.0	0.8752	0.622	1.0000	2.92	2.92
20	B	23.4	0.8747	0.616	0.9893	3.59	3.55

*Corrected to density of dispersing medium at 23°C. and to viscosity of benzene at 23°C. assuming d = 1.25 g/cm³.
†B = benzene, C = carbon tetrachloride.
‡Correction factor:

$$\left(\frac{v_t}{d - d_t}\right) \left(\frac{d - d_{23}}{v_{23}}\right)$$

for line 2: $\left(\frac{0.611}{1.25 - 0.8741}\right) \left(\frac{1.25 - 0.8752}{0.622}\right) = 0.9796$

**Approximate temperature.
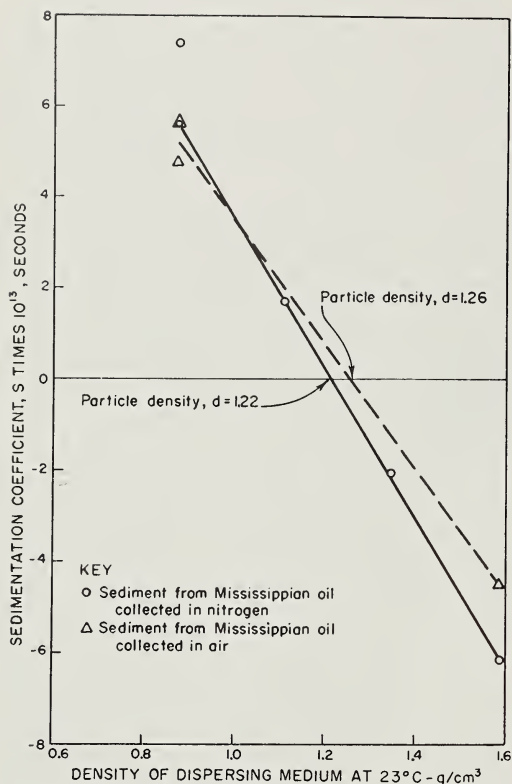
Fig. 23.—Corrected sedimentation coefficients versus density of dispersing medium.

of benzene at 23°C. and 1 atmosphere was taken as an arbitrary reference state, and all results were further corrected as shown in table 21 to yield $(s°)_c$.

Figure 23 shows the final plot of corrected sedimentation coefficients. It will be noted that the data for sediment that was centrifuged from Mississippian crude oil collected under nitrogen give an excellent correlation and establish that the true particle density is 1.22 g/cm³. Only one point, $(s°)_c = 7.4 \cdot 10^{-13}$ sec., is in disagreement, and it is obviously so out of line with all the other data for sedimentation in benzene (table 21) that no weight was given this result. As previously discussed, changing d from 1.25 to 1.22 has a negligible effect on correction factors for compressibility (table 7). The same is true for the temperature-viscosity correction factors listed in table 21.

Sedimentation coefficients calculated from the basic data of figures 14, 15, and 16, also

are included on figure 23 to show a tentative correlation for the density of particles centrifuged from Mississippian crude oil that was collected in air. These data indicate an effective particle density of 1.26 g/cm.³, but this result is based upon only two different dispersion media.

Calculation of Particle Size and Molecular Weight

Particle size may be calculated from equation 3 if the assumption of spherical shapes is accepted. Such a shape seems to be strongly indicated from the work of others (Pfeiffer and Saal, 1940; Höppler, 1941). By integrating and rearranging equation 3, the following may be obtained:

$$r^2 = \frac{4.5 \ v}{d - d_m} \cdot \frac{\ln \ x_2 - \ln \ x_1}{w^2 \ (t_2 - t_1)} \qquad (17)$$

and as

$$s = \frac{\ln \ x_2 - \ln \ x_1}{w^2 \ (t_2 - t_1)}$$

equation 17 can be shortened to

$$r = \left(\frac{4.5 \ v \ s}{d - d_m} \right)^{\frac{1}{2}} \qquad (18)$$

By use of equation 18, the particle radii were calculated for each run and are listed in table 22.

The molecular weight of a spherical particle may be calculated from the standard formula:

$$M = \frac{4}{3} \pi \ r^3 \ d \ N \qquad (19)$$

where $N =$ Avogadro's number, $6.023 \cdot 10^{23}$. Using the radii obtained from equation 18, molecular weights were computed and are included in table 22.

OTHER ANALYTICAL STUDIES TO CHARACTERIZE CRUDE OIL SEDIMENT

Elemental Analyses

Elemental analyses were made by Donald R. Dickerson, of the Geological Survey, on three samples, using standard micro-analytical techniques: 1) original Mississip-

TABLE 22.—CALCULATED PARTICLE SIZES AND MOLECULAR WEIGHTS

Crude oil	$(s°)_e$ x 10^{13} at 23°C. sec.	d g/cm.³	d_m at 23°C. g/cm.³	r Å*	M
Mississippian	7.40	1.22	0.8752	24.7	46,400
Mississippian	5.61	1.22	0.8752	21.3	29,700
Mississippian	−6.12	1.22	1.5882	21.5	30,600
Mississippian	1.75	1.22	1.1135	21.4	30,200
Mississippian	−2.04	1.22	1.3510	20.9	28,100
Mississippian	5.62	1.26	0.8752	20.2	26,200
Mississippian	4.77	1.26	0.8752	18.6	20,500
Mississippian	−4.48	1.26	1.5882	19.5	23,600
Pennsylvanian	4.99	1.26	0.8752	19.1	22,200
Devonian	4.10	1.22	0.8752	18.2	18,600
n-Heptane-Miss.	2.92	1.2†	0.8752	15.9	12,800
Benzene-Miss.	3.55	1.2†	0.8752	17.5	17,000

*v = 0.622 cp. in all calculations.
†Assumed.

pian crude oil, 2) sediment centrifuged from the oil, and 3) sediment centrifuged from a 1:1 mixture (by volume) of normal heptane and this oil. The results are presented in table 23.

TABLE 23.—ELEMENTAL ANALYSES OF MISSISSIPPIAN CRUDE OIL AND OF SEDIMENTS OBTAINED BY CENTRIFUGATION

Element	Crude oil	Sediment from	
		Oil	Heptane-oil mixture
Carbon	85.27%	88.21%	88.46%
Hydrogen	12.78	8.12	8.92
Nitrogen	0.55	1.71	1.23
Sulfur	0.26	0.62	0.55
Chlorine*	trace	1.07	0.72
Ash†	nd	nd‡	nd
Total	98.86%	99.73%	99.88%
C/H ratio	0.56	0.91	0.83

*Probably from salt.
†Not detected in C-H determinations.
‡About 2% ash obtained with sulfuric acid.

Trace Metal Determinations

The three Illinois crude oils were examined for trace amounts of nickel, vanadium, and copper by Dr. Kozo Nagashima of the Tokyo University of Agriculture and Technology, who was temporarily on the staff of the Geological Survey during 1955-57. The crude oil samples were prepared by a thorough washing with distilled water followed by centrifugation at 1550 r.p.m. to remove any brine or suspended contaminants. To a 100 g. sample of crude oil was added a known amount of a cobalt solution (internal standard) plus 100 ml. of concentrated sulfuric acid and about 5 ml. of concentrated nitric acid. This mixture was coked, ashed at 550°C., and the residue dissolved in hydrochloric acid. The solution was diluted with distilled water to 10 ml. and excited by spark, using a rotating graphite electrode. Measurements were made by comparing the line intensity of copper, nickel, and vanadium with that of cobalt. The results are shown in table 24. Details of the method of analysis have been presented by Nagashima and Machin (1957).

As measurable amounts of metals were found in the crude oils, one two-day preparative centrifugation run was made on two samples of Mississippian oil, one collected in air and the other in nitrogen, to obtain

Table 24.—Trace Amounts of Nickel, Vanadium, and Copper in Illinois Crude Oils

Crude oil	Nickel mg/100g	Vanadium mg/100g	Copper mg/100g
Pennsylvanian	0.24	0.17	0.027
Mississippian	0.22	0.10	0.049
Devonian	0.069	0.037	0.009

enough sediment for trace element determinations. The metals were prepared for analysis by the same procedure outlined above. Sediment centrifuged from a 1:1 mixture (by volume) of normal heptane and Mississippian crude oil also was analyzed. The results are summarized in table 25. Copper is omitted because there is some doubt that measurements of this trace metal have real meaning (Witherspoon and Nagashima, 1957).

Absorption Spectra

As mentioned previously, trace metals such as nickel and vanadium have been found complexed with porphyrins in crude oil and various bituminous rocks by a number of workers in many parts of the world (Treibs, 1935; Glebovskaya and Vol'-Kenshstein, 1948; Blumer, 1950; Skinner, 1952; Dunning et al., 1953; Scott et al., 1954; and Radchenko and Sheshina, 1955). In view of the trace amounts of nickel and vanadium found, it was decided to determine whether porphyrins are present in the Illinois crude oils, particularly in the centrifuged sediment where the metals are concentrated 20- or 30-fold (table 25).

In accordance with procedures that have been outlined by Skinner (1952) and Dun-

ning et al. (1953), sediment that had been centrifuged from the Mississippian oil was refluxed with absolute ethanol until a sufficient sample of alcohol-soluble material was obtained for visible absorption work. The alcohol-insoluble residue also was examined. Both samples were scanned in chloroform from 500 to 600 millimicrons (fig. 24). Mou-shu Chao, of the Uni-
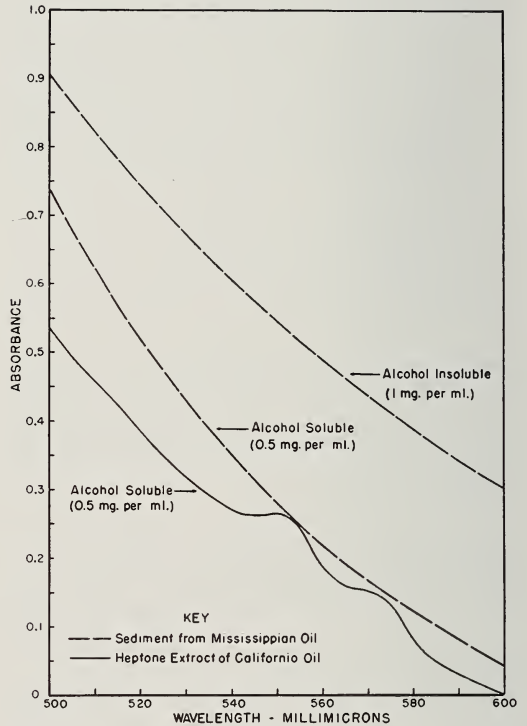
Fig. 24. — Visible absorption spectra of sediment centrifuged from Mississippian oil and of heptane extract of California oil. Scanned in chloroform.

Table 25.—Trace Amounts of Nickel and Vanadium in Sediment Centrifuged from Mississippian Crude Oil

Oil collected under	Oil, gm.	Sediment analyzed, gm.*	Metals in sediment†		Concentration in sediment‡	
			Nickel, mg/100g	Vanadium, mg/100g	Nickel, times	Vanadium, times
Air	55	0.601	5	2	20	20
Nitrogen	55	0.618	6	2	30	20
Heptane-oil	38	0.543	7	2	30	20

*Centrifuged from oil after 53 hours at 30,000 r.p.m. and approximately 20°C.
†Values shown give orders of magnitude only.
‡Approximate times more concentrated than in original oil.

versity of Illinois Chemistry and Chemical Engineering Department, obtained the visible absorption spectrograms shown here and elsewhere, using a Model 14 Cary Recording Spectrophotometer.

It was anticipated from the literature cited above that, if nickel and vanadium porphyrins were present, prominent absorption peaks should appear within the range of wavelengths indicated on figure 24. However, there is no indication of any absorption for either the alcohol-soluble or -insoluble extracts of the Mississippian sediment.

To check the over-all procedure, a normal-heptane precipitate of the California crude oil was obtained by essentially the same method utilized by Dunning et al. (1953) in their investigations on this oil. An alcohol extract of this heptane precipitate was scanned in chloroform and the absorption curve is included on figure 24. The two prominent peaks at about 550 and 570 and a minor one at about 510 millimicrons are in good agreement with the results obtained by Dunning et al. They have presented adequate proof that the 550 and 510 bands indicate a nickel porphyrin and the 570 band a vanadium porphyrin in this California crude oil.

As the sediment centrifuged from the Mississippian oil represents about one percent of the crude, an attempt also was made to identify porphyrins in the rest of the crude oil by infrared absorption. The infrared spectra were obtained by James J. Brader, Spectroscopist in the University of Illinois Chemistry and Chemical Engineering Department, using a Model 21 Perkin-Elmer Recording Infrared Spectrophotometer. Brader also assisted in interpreting the results.

To obtain reference data two samples, one a very pure nickel porphyrin complexed from a mesoporphyrin IX dimethyl ester and the other a vanadium porphyrin extracted from crude oil, were obtained through the courtesy of Dr. H. N. Dunning. Visible absorption spectra for these two porphyrins are shown in figure 25 to demonstrate their identity. The nickel porphy-
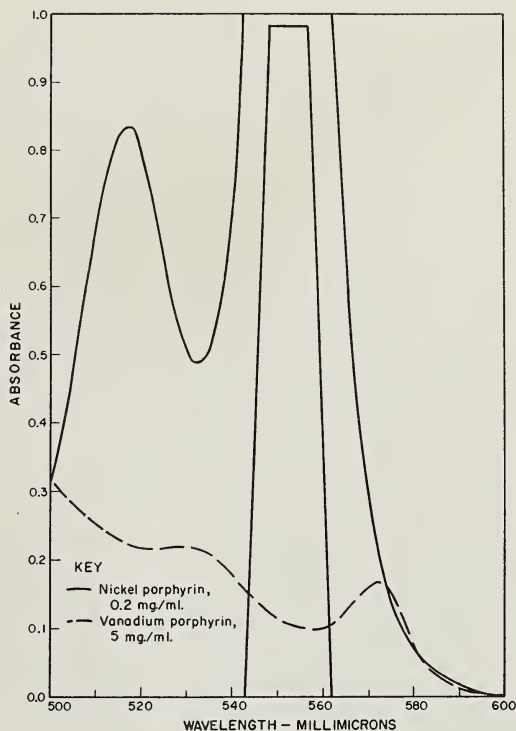
Fig. 25.—Visible absorption spectra of nickel and vanadium porphyrins. Scanned in chloroform.

rin was run in a relatively low concentration of 0.2 mg./ml. of chloroform, yet its absorption peak at 552 millimicrons was so intense that both recording pens of the Cary spectrophotometer went off scale. This major peak and the less intense one at about 515 millimicrons are standard reference bands for nickel porphyrin, as are the 570 and 530 bands obtained for the vanadium porphyrin (see literature cited above).

Infrared absorption data for the nickel and vanadium porphyrins are shown in figures 26A and 26B, respectively. For the most part, the absorption bands of these two figures are not attributable to porphyrins alone. One rather weak band at about 10 microns, however, may be attributable to the porphyrins. It is present in the spectra of both figures, and also is easily recognized in figure 26C, which is the spectrogram for the alcohol-soluble portion of a heptane extract of the Cali-
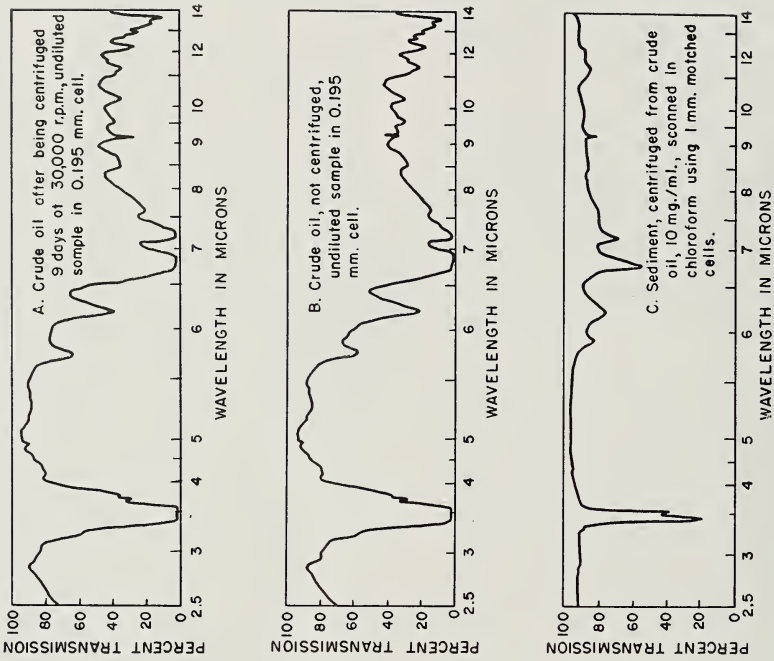
Fig. 27.—Infrared absorption spectra of Mississippian crude oil and sediment using NaCl prism.

A. Crude oil after being centrifuged 9 days at 30,000 r.p.m., undiluted sample in 0.195 mm. cell.

B. Crude oil, not centrifuged, undiluted sample in 0.195 mm. cell.

C. Sediment, centrifuged from crude oil, 10 mg./ml., scanned in chloroform using 1 mm. matched cells.
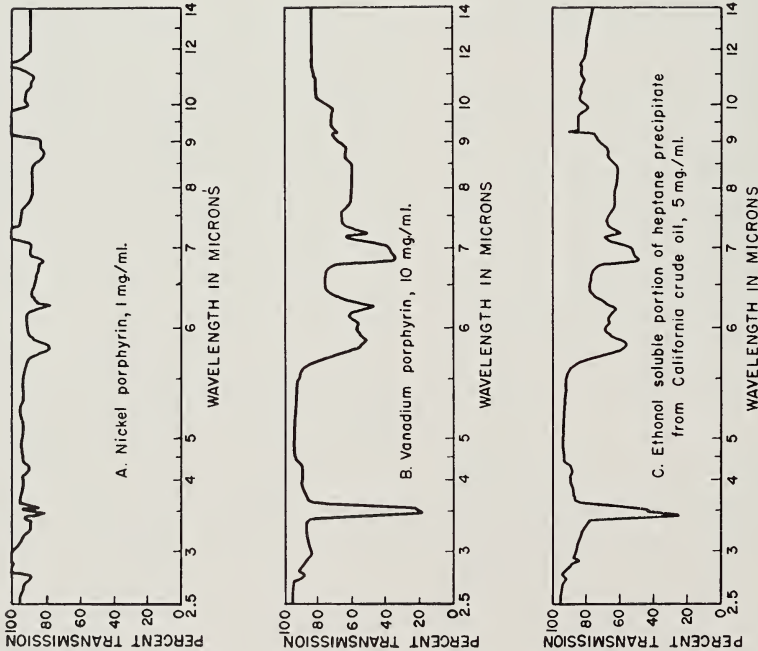
Fig. 26.—Infrared absorption spectra of metal porphyrins. Scanned in chloroform using NaCl prism and 1 mm. matched cells.

A. Nickel porphyrin, 1 mg./ml.

B. Vanadium porphyrin, 10 mg./ml.

C. Ethanol soluble portion of heptane precipitate from California crude oil, 5 mg./ml.

fornia crude oil, previously shown to contain both nickel and vanadium porphyrins.

Infrared absorption spectra for Mississippian crude oil that had been centrifuged 9 days at 30,000 r.p.m. are shown in figure 27A. For comparison, absorption spectra on uncentrifuged oil are shown in 27B. These two samples were scanned without dilution. Figure 27C shows absorption spectra obtained for Mississippian sediment scanned in chloroform. It will be noted that the 10-micron band mentioned above is absent in all three of these spectrograms.

Electron Microscopy

As mentioned previously, Preckshot et al. (1943), Katz and Beu (1945), and Skinner (1952) have attempted to use the electron microscope to find asphaltic materials of colloidal dimensions in crude oil, without success. When they treated the oil in some fashion, such as diluting it with a solvent or subjecting it to an electric field, they caused particles to form, in some instances with dimensions of 100 Å or larger. After examining a large number of samples, Katz and Beu (1945) concluded that if asphaltic materials exist as colloidal particles in petroleum, they must be less than 65 Å in diameter.

As the analytical centrifugation work demonstrated that sediment centrifuged from all three Illinois crude oils is about 40 Å in size when dispersed in benzene, carbon tetrachloride, or mixtures of the two, it was decided to examine the sediment at the high magnifications obtainable with the electron microscope. Dr. Albert E. Vatter, Electron Micrographer in the University of Illinois Chemistry and Chemical Engineering Department, did all the microscopy work reported here, using an RCA—EMU—2e electron microscope. He also assisted in interpreting the results.

Benzene dispersions of sediment centrifuged from the Mississippian oil were placed directly on a collodion film supported by a 200-mesh grid and allowed to dry. In the electron microscope, the sediment appeared primarily as irregular aggregations of many different sized particles, as shown in plates 2A and 2B. The size of these aggregates is 1 to 2 microns. Clay-like hexagonal particles, 0.5 to 3 microns in size, were also occasionally observed and plate 2C is the best example.

An attempt was made to avoid particle aggregation of the organic matter by another technique. A very low concentration of sediment in ethyl ether (about 0.1 mg/ml.) was sprayed with a low-velocity atomizer onto a freshly cleaved sheet of muscovite. After it dried, the material was shadowed with platinum at an angle of about 4 to 1 (so that any shadows produced would be about four times the height of the specimen). The thickness of the platinum film was 10 to 20 Å. The shadowed specimen was then backed up with a carbon film, about 100 Å thick, applied normal to the surface. This pseudo-replica was removed by floating it away from the specimen with water, and mounted on the usual grid-supported collodion film.

Sediment prepared in this way revealed numerous particles of the order of 50 to 100 Å, and a typical example at 100,000 magnifications is shown in plate 2E. At this magnification, 1 mm. on the photograph is equivalent to 100 Å. It will be noted that, aside from the prominent accumulation on the right hand side of the photograph, more than 90 percent of the particles are less than 100 Å, and most of them are of the order of 50 Å in size. The prominent accumulation also has particles as small as 50 Å, but there seems to be a larger proportion of particles around 100 Å. In many places, these larger sizes appear to be clusters of several smaller particles. The shadow of this accumulation is about 300 Å long, which indicates an average height of about 80 Å. Resolution of 20 to 30 Å may be observed at many points.

For particle sizes in this range it is important to have a background, or substrate, whose texture does not approach that of the material to be examined. Freshly cleaved muscovite was shadowed, by the same procedure outlined above, and plate 2D is an electron micrograph of the mica surface enlarged to 100,000 magnifications.

The surface is essentially featureless, at least to particles of 10 Å or larger. Therefore, the texture shown in plate 2E is that of the sediment and not of the background.

It will be remembered that a thin film of grayish-white material was noted on the inside of the lusteroid tubes at the end of the preparative centrifugation runs on the Illinois crude oils. This material was not soluble in benzene and was considered to be inorganic. As the amount of film was too small to examine even by microanalytical methods, it was examined with the electron microscope.

The lusteroid tube was cut open and the interior film shadowed with a chromium metal coating, which was given further support by a film of carbon applied normal to the surface. The chromium-carbon film was removed from the tube material by placing it in propylene oxide, tetrahydrafuran, 3-pentanone, and various mixtures of these three solvents. The pseudo-replicas were then placed on grid-supported, collodion films for examination. The polymer material of the tube was not completely dissolved, however, and remnants remained on the film that greatly hampered the microscopic investigations.

Many different-shaped particles were observed, most of which were not identified. However, a significant percentage of hexagonal platelets (pls. 3A and 3C), similar to that shown in plate 2C, were found and are believed to be kaolinite. Lath-shaped particles were also observed (pls. 3B and 3D) and possibly are clay minerals, but this is less certain. The particles shown in plate 3 do not have any shadow, which suggests that they were imbedded in the surface of the plastic tube.

After the California crude oil was centrifuged, a significantly larger amount of the grayish-white, inorganic film was found than in the Illinois crude oils. This material was mounted directly on grid-supported, collodion films for examination. Again a number of different shaped particles were observed, among them a significant amount of lath-shaped particles (pls. 3E and 3F), about one-half micron in size.

X-ray Analysis

Eilers (1949) has shown that the ratio of intensities of the 4.5 to 3.5 Å reflections as obtained by x-ray analysis provides a rough indication of the structural nature of asphaltenes. The 3.5 Å reflection is caused by aromatic ring structures in the asphaltene, and the 4.5 Å reflection is due to aliphatic chain structures. Therefore, as the ratio increases, the material is more aliphatic; conversely, when the ratio decreases, the material is more aromatic.

One sample of sediment centrifuged from Mississippian crude oil was evaporated on a glass slide from a benzene solution and x-rayed by Dr. W. F. Bradley of the Geological Survey with a GE diffractometer and filtered copper radiation.

A smoothed trace of the x-ray spectrogram is shown in figure 28, and it will be noted that a broad band of radiation was obtained between 2θ angles of 15 and 35 degrees. The ratio of the intensities of the 4.5 to 3.5 Å reflections is about 0.9. Approximately the same results were obtained with another sample of sediment that was centrifuged from a 1:1 mixture (by volume) of normal heptane and this same crude oil.
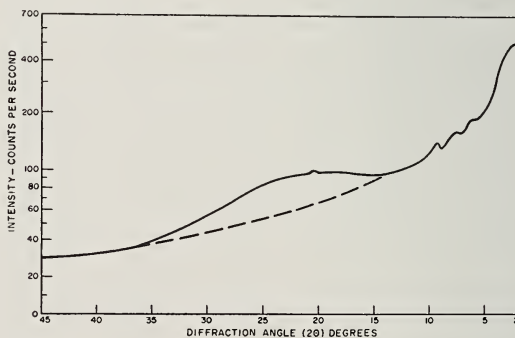
Fig. 28.—X-ray spectrogram of sediment centrifuged from Mississippian crude oil.

CENTRIFUGAL FRACTIONATION OF CRUDE OIL AND PHYSICAL PROPERTIES OF LAYER-FRACTIONS

In the preparative centrifugation experiments that originally were designed to recover colloidal-sized particles from the

crude oil, it was noted that at the end of the two-day runs the supernatant liquid was beginning to exhibit evidences of fractionation. The topmost layers of the liquid were distinctly different in color and seemed to be less viscous than the bottom layers. To get some quantitative data on whether or not centrifugal fractionation was actually occurring, a 59-hour preparative centrifugation run was made on the Mississippian oil. At the end of the run, the centrifuge tubes were frozen and divided into four almost equal portions by the procedure previously described. The collection of sediment at the bottom of the tube also was separated from the bottom quarter so that the sediment would not remix with this fraction.

These four fractions and the bottom sediment were then examined to determine if there were measurable differences in their physical and chemical properties. Table 26 shows the color, density, and viscosity of the four fractions at 25.0°C. Densities were measured with a Westphal balance and viscosities were measured with an Ostwald viscosimeter pipette in accordance with ASTM D445-53T procedure.

TABLE 26.—COLOR, DENSITY, AND VISCOSITY OF CENTRIFUGALLY FRACTIONATED MISSISSIPPIAN CRUDE OIL AT 25°C.

Frac-tion*	Color†		Density at 25°C. g/cm.³‡	Viscosity at 25°C. cp.**
	Reflected	Transmitted		
1	lt. green brown	lt. orange brown	0.8315	4.57
2	dk. green brown	dk. red brown	0.8365	4.95
3	black	black	0.8407	5.43
4	black	black	0.8461	6.26
0	black	black	0.8408	5.48

*1—top quarter, 2—second quarter, 3—third quarter, 4—fourth quarter, and 0—crude oil before centrifuging.
†Color to transmitted and reflected day light.
‡Average of three determinations.
**Average of three to five determinations.

These four fractions and the bottom sediment were further investigated by measuring the interfacial tensions of 1.0

and 0.1 weight percent solutions in benzene against water at 25.0°C. These measurements were made with a standard ring-type tensiometer and in accordance with ASTM 971-50 procedure. The results are summarized in table 27.

TABLE 27.—INTERFACIAL TENSIONS OF SOLUTIONS OF CENTRIFUGALLY FRACTIONATED MISSISSIPPIAN CRUDE OIL IN BENZENE AGAINST WATER AT 25°C.

Fraction*	Interfacial tension†	
	1.0% solution, dynes/cm.	0.1% solution, dynes/cm.
Benzene	33.4‡	33.3‡
1	32.9	33.0
2	32.4	33.1
3	32.2	33.0
4	31.7	33.0
5	—	29.6
0	32.1	33.0

*1—top quarter, 2—second quarter, 3—third quarter, 4—bottom quarter, 5—sediment at very bottom of tube, 0—crude oil before centrifugation.
†Average of duplicate determinations. Solutions are percent by weight in benzene.
‡Benzene against water for reference purposes.

As these investigations definitely indicated that the crude oil was being fractionated, one analytical centrifugation run was attempted on the Mississippian crude oil at about 60,000 r.p.m. and approximately 23°C. After 15 hours, there was a noticeable clarification in the top one-eighth of the oil, and after almost 40 hours the top one-fourth of the cell was definitely clearing. Attempts to record this progressive clarification were unsuccessful, however, because not enough light could be transmitted to the photographic film through the color remaining in the supernatant liquid. A longer run should have improved this situation, but the analytical ultracentrifuge requires constant supervision and runs of several days were not feasible.

On the other hand, the preparative centrifuge has automatic speed and temperature controls that enable one to make runs

of almost any duration. Therefore, during the twelve-day run that was made to determine the maximum sediment obtainable by centrifugation, observations also were made on the supernatant liquid.

Plate 4A is a photograph of a colored exposure* of uncentrifuged crude oil and the same oil after centrifugation for twelve days at 30,000 r.p.m. and 20°C. In this photograph the samples were still in the plastic centrifuge tubes, and both tubes were illuminated from the same sources of transmitted and reflected light. The top of the tube is nearest the center of rotation during centrifugation, and clarification therefore starts from the top.

It will be noted in plate 4A that the centrifuged oil has separated into three color zones. In transmitted light, the top zone was bright yellow, the middle zone brick red, and the lower zone black, which obscures the location of the sediment that had collected at the bottom. Similar results were obtained after nine days of centrifugation, except that the boundaries between the color zones were about two percent higher in the tube.

Three fractions were separated from the supernatant oil shown in plate 4A by removing, with a hypodermic needle, about one-tenth of the volume of the tube from the top (yellow zone), the middle (red zone), and the bottom (black zone). This was repeated in three other tubes that had been centrifuged for twelve days, and the separated fractions were combined as shown on plate 4B.

CENTRIFUGATION OF HEPTANE-OIL MIXTURES

In the preliminary investigations with the preparative centrifuge on mixtures of normal heptane and Mississippian crude oil, it was noted that discrete bands of color developed shortly after the tubes were removed from the rotor at the end of a run. These bands were a transparent light reddish orange at the top (nearest the center of rotation) and became progressive-

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*Colored prints are included in the original thesis.

ly darker toward the bottom where the mixture was as black and opaque as the original solution. The bands were not stable and gradually disappeared within about a half hour. This phenomenon seemed to occur when the heptane-oil ratio was around 1.0, but for some unknown reason the banding could not always be reproduced.

Plate 4C is a black and white photograph of these bands as they appeared with two different heptane-oil mixtures after a 58-hour run at 30,000 r.p.m. The mixture in the centrifuge tube on the left contained a 1:1 ratio of heptane to oil by volume, and the tube on the right contained a 2:1 mixture. Nine to ten bands are easily distinguished in either tube, and it will be noted that with greater dilution the bands are more easily observed throughout the length of the tube.

As these tubes were centrifuged in an angle-head rotor, there was a possibility that this curious banding could be related in some way to convection currents occurring at the end of the run when the density gradient was reduced and the tube changed to a vertical position for examination. To check on this point, fresh mixtures of the same two heptane-oil ratios were centrifuged for 60 hours at 28,000 r.p.m. in a swinging bucket rotor.

In this type of rotor, the centrifuge tube is aligned in the direction of the centrifugal field during operation. Therefore, there is less disturbance to sedimentation and material does not accumulate along the side walls. Plate 4D shows the two centrifuge tubes just a few minutes after they were removed from the rotor. The tube on the left, which shows no bands, contained a 1:1 heptane-oil mixture, and the other tube, which shows eight bands, contained a 2:1 mixture. The contents of these two tubes were later mixed to their original color and recentrifuged for 96 hours in the same rotor, but with different results. The 1:1 mixture again showed no bands, and the 2:1 mixture had only one or two very poorly developed bands.

DISCUSSION OF RESULTS

Results From the Physico-Chemical Standpoint

Particles dispersed in the crude oils of this investigation were segregated by the imposed gravitational fields, and they fall into two broad classifications, organic and inorganic. The organic particles will be considered first and the inorganic particles will be discussed later from the geologic standpoint.

Organic particles of colloidal dimensions were segregated in the preparative centrifuge experiments on the Illinois crude oils because their size and density were sufficiently greater than that of the media in which they were dispersed. Prolonged experiments on the Mississippian crude oil have further demonstrated that there are at least three general groups of discrete particles dispersed in the oil: a group, referred to as *sediment,* that can be centrifuged completely out of suspension; a second group, called here *black particles*, that apparently contains the remaining black coloring matter in the oil (pl. 4A) and can almost be removed from suspension at 30,-000 r.p.m.; and a third group, called here *red particles,* containing other pigmented materials that in transmitted light have a distinct reddish color. The classification is based on the fact that no sediment is recovered after four days of centrifugation at 30,000 r.p.m. (fig. 8), and on the appearance of a rather sharp boundary between the black and the red particles and a less well-defined boundary between the red particles and the yellow supernatant liquid (pl. 4A). As there is still considerable fluorescent matter left in the supernatant liquid, it would not be surprising to find other groups of discrete particles upon the application of higher gravitational fields. This is a point that merits further study.

The fact that these three groups of particles were segregated under the influence of the imposed gravitational field means that they are each different from the other in size and/or density. As the sediment comes down first, it should contain the largest particles of the greatest density.

Either or both of these factors presumably diminish for the black particles and diminish further for the red particles, as will be shown later. Thus, behavior in sedimentation experiments such as these provides a means of categorizing dispersed systems in crude oil.

Further work was needed, however, to define the properties of the segregated particles more specifically. The sediment was obviously the material on which detailed investigations could be carried out most conveniently because it was readily separated from the oil. Therefore, the following discussion will be largely devoted to the nature of this sediment, and the other particles will be treated subsequently but only briefly.

The organic sediment centrifuged from the Mississippian crude oil is an asphaltic material that falls under the very broad classification of asphaltenes. It is coagulated in paraffin hydrocarbons such as normal heptane but is completely dispersed in benzene. When separated from crude oil and dried, it is a black solid that decomposes without melting upon being heated. These are typical criteria of the asphaltenes.

As to the solubility of this material, Nellensteyn (1923, 1931, 1938) has reported in his studies of the colloidal nature of asphalt that organic solvents that are miscible with the maltenes and whose surface tensions are above 24-26 dynes/cm. are good peptizers for the asphaltenes. More recently, Eilers (1949) has proposed another criteria for solubility based on internal pressure. He defines internal pressure as the product of surface tension and the reciprocal of the cube root of the molecular volume of the solvent in question. Eilers has shown that asphaltenes are completely dispersed in all non-polar liquids whose internal pressures are larger than 4.5. From either basis, normal heptane is not a good peptizer because its surface tension at 25°C. is 19.9 dynes/cm. and its internal pressure is 3.77, whereas benzene, with a surface tension of 28.2 dynes/cm. and an internal pressure of 6.32, is an excellent disperser of the asphaltenes (Eilers, 1949, p. 1199).

Another useful criteria is the C/H ratio. Aliphatic paraffin hydrocarbons have a ratio approaching 0.5, whereas aromatic hydrocarbons such as benzene (C/H = 1.0) and napthalene (C/H = 1.25) have much higher values. The asphaltenes are believed to be a combination of both types of hydrocarbons, so a measure of C/H ratio indicates whether the structure is predominantly aliphatic or aromatic. The C/H ratios for asphaltenes range from 0.61 to 1.32, but in general are around 0.9 for material that has not been subjected to thermal cracking (Saal et al., 1946; Eilers, 1949). The elemental analyses in table 23 indicate a C/H ratio of 0.91 for sediment from straight crude oil and 0.83 for sediment centrifuged from a mixture of normal heptane and crude oil. As is evident in table 11, the addition of heptane to crude oil produced significantly more sediment for a given period of centrifugation. The lower C/H ratio of this sediment is therefore an indication that more aliphatic type materials were collected using heptane.

As discussed previously, Eilers (1949) has shown from x-ray studies that asphaltenes are a mixture of aliphatic chains and aromatic ring structures, and this is roughly indicated by the ratio of intensities that occur at 4.5 Å and 3.5 Å, respectively. The 0.9 ratio obtained in this work is in good agreement with his findings.

A further indication of the aliphatic-aromatic nature of asphaltenes is evident in the infrared absorption data of figure 27C. The prominent absorption bands at about 3.4, 6.8, and 7.2 microns are due to aliphatic chain structures, and the broader band at 6.2 microns is caused by aromatic ring structures. In addition, these asphaltenes contain partly oxidized molecules (the carbonyls) as is indicated by the absorption band at 5.9 microns. It will also be noted that all of these absorption bands are present in the crude oil spectrograms of figures 27A and 27B, and similar observations have been reported for other crude oils (Stevens et al., 1956). This is evidence of the complicated chemical nature of petroleum.

The fact that asphaltenes comprise the sediments centrifuged from the Mississip-

pian oil is consistent with the fact that Illinois oils are generally somewhat asphaltic (Gruse and Stevens, 1942, p. 10; Rees et al., 1943). The material centrifuged from the Devonian and Pennsylvanian crude oils had the same appearance, the same solubility characteristics, and the same particle size as the Mississippian sediment. It is therefore concluded that the materials separated from the Illinois crude oils in the preparative centrifuge are asphaltenes.

The above discussion concerns the nature of the sediment as it can be determined from standard methods of analytical chemistry. With the aid of the ultracentrifuge, however, one can obtain additional information of fundamental value, and this was the purpose of the detailed analytical centrifugation experiments.

It has been shown by others (Sharp et al., 1944; Schachman and Lauffer, 1949) that a plot of s (when properly corrected) vs. d_m should yield a straight line if the dispersing medium has no effect on the size, shape, and density of the particles. Furthermore, the extrapolation to s = 0 should give the true density of particles as long as the density of any solvated material is the same as that of the dispersing agent. In calculating the size of the particles from s, however, the results may be somewhat smaller than the true value because experimental s is dependent on the hydrodynamic size of the particle (i.e., the size of the solvated particle).

The curve shown on figure 23 for the sediment that was centrifuged from the Mississippian oil (collected in nitrogen) shows a linear dependence between s and d_m, and this indicates that the four different media used had little or no effect on the asphaltene particles. One might also infer that changes in the degree of solvation was not an appreciable factor in any of these various dispersions. By interpolation, the true density of these particles is 1.22 g/cm³. For the other sediment that was centrifuged from oil collected in air, the indicated density is 1.26 g/cm.³, or about 3 percent higher. This latter value, however, is based on results with only two

different dispersing media, and further work would be required to establish this difference.

The shape of dispersed asphaltene particles has been a matter of conjecture for some time. On the basis of detailed studies of the rheological properties of asphalt, Pfeiffer and Saal (1940) and Höppler (1941) have postulated a spherical shape for the asphaltenes. More recently, Eckert and Weetman (1947) have assumed a linear shape for particles of this material although such a configuration has not been demonstrated.

As may be seen in the electron micrograph of plate 2E, the preponderance of particles are essentially round in outline. Ethyl ether was used in the preparation of this material, and some aggregation may have resulted because this solvent is a poor peptizer of the asphaltenes. The only suggestion of linear shapes in plate 2E is in the prominent accumulation where close inspection will reveal an apparent agglomeration of rounded particles in many instances. It was therefore concluded that spherical shape was a reasonable assumption to adopt for the asphaltene particles of this work.

On the basis of this assumption, the Mississippian sediment was categorized as being asphaltene particles of about 40 Å in diameter and having a density of 1.22 g/cm.^{3} and a molecular weight of about 30,000 (table 22). It should be emphasized that these results were obtained whether the sediment was dispersed in benzene, carbon tetrachloride, or mixtures of the two, which, of course, is the implication of the linear dependence of s and d_m. Apparently, the particles were completely peptized in the variety of solvents used. According to the theories of Nellensteyn (1931) and Eilers (1949), this is to be expected for benzene, but Nellensteyn regards carbon tetrachloride as intermediate between a flocculating and peptizing agent. Thus, these results suggest that the asphaltenes were in their highest natural state of dispersion, or in other words, 40 Å is an average unit particle dimension.

It is also significant that the asphaltenes centrifuged from the Pennsylvanian and Devonian crudes have almost the same sedimentation coefficients when dispersed in benzene as that of the Mississippian oil. It is reasonable that the density of these particles should be practically the same as that of the Mississippian oil, so the calculated particle dimensions are again essentially 40 Å.

In crude oil, the asphaltenes of these three oils are probably peptized by the maltenes in much the same way that Pfeiffer and Saal (1940) have proposed for their existence in asphalt. The asphaltene particles seem to have a fixed size when dispersed in various media, and it is postulated that the unit dimensions of these particles in their natural state in petroleum are approximately the same as in the solvents used in this work.

Confirmation of the above conclusion is indicated by the following. A rough approximation of the particle size of the "sediment" as it occurs in crude oil may be calculated from the fact that after four days (fig. 8) no more sediment was obtained in the preparative centrifuge. During this time interval, the sediment moved the maximum radial distance of the rotor, from 6.3 to 9.4 cm., at 30,000 r.p.m. Assuming a viscosity of 10 cp. and a density of 0.84 g/cm.^{3} for the crude oil, the minimum particle diameter is calculated to be approximately 70 Å, which is the same order of magnitude obtained above. By analyzing the low-angle x-ray scattering intensities of asphaltenes, Alexanian and Louis (1950) obtained an average particle size of the order of 85 Å.

It will be recalled that Katz and Beu (1945) postulated on the basis of numerous electron microscopic studies that, if such particles are present in untreated asphalts and crude oils, they must be less than 65 Å in diameter. The electron micrograph in plate 2E reveals many particles of the order of 50 Å in diameter although there probably was some degree of aggregation resulting from the use of ethyl ether. In any event, all of the above results are in general

agreement with the 40 Å value obtained by analytical centrifugation. The pore sizes of most collodion membranes are significantly greater than 40 Å, so it is not surprising that ultrafiltration and dialysis experiments with this membrane have failed to reveal the presence of colloidal-sized particles in asphaltic materials.

Molecular weights for asphaltenes as measured by the cryoscopic method vary from 2,000 to 30,000 (Saal et al., 1946), but there is some doubt whether such methods can be applied to the asphaltenes. Hillman and Barnett (1937) concluded from their work with this method that the average molecular weight of ill-defined mixtures, such as asphaltenes, cannot be accepted as absolute, because solutions of these fractions probably depart appreciably from the ideal solution law.

Eckert and Weetman (1947) were able to get reliable data for the maltenes using the cryoscopic method but report that the method does not lend itself readily to obtaining molecular weights of asphaltenes. They have therefore attempted to apply Staundinger's relationships between viscosity and molecular weight of linear macromolecules and arrived at values of the order of 1000 for the molecular weight of asphaltenes. As mentioned previously, a linear configuration for the asphaltenes has not been demonstrated and Eilers (1949) shares this viewpoint. Furthermore, in evaluating the constants for the Staundinger equations, Eckert and Weetman used data obtained on the maltenes but were unable to demonstrate conclusively that such constants apply for the asphaltenes. Thus, molecular weights for asphaltenes that have been determined by cryoscopic methods or by the application of the Staundinger relationships, as employed by Eckert and Weetman, are of doubtful reliability.

Using Langmuir's methods, Pfeiffer and Saal (1940) studied monomolecular films of asphaltenes and obtained molecular weights ranging from 80,000 to 140,000, but they consider their results too high. Saal et al. (1946) believe the real values for the molecular weights are between the

maximum values obtained by Langmuir's methods and the minimum values indicated by cryoscopic methods. The molecular weight of 30,000 determined in this work supports that viewpoint, but until the degree of homogeneity of asphaltenes from a variety of sources has been defined, it seems quite possible that there may be a significant range in the molecular weights of such materials. It is believed that the ultracentrifuge could be used very effectively in evaluating this fundamental property of the asphaltenes.

In view of the finding that nickel and vanadium are concentrated 20 to 30 times in the sediment (table 25), it was surprising that no metal-porphyrins could be found. However, metals are probably complexed with organic compounds in petroleum in many different ways (Dodd et al., 1952; Dunning et al., 1953, 1954). Radchenko and Sheshina (1955) have recently shown from studies of a large number of Russian crude oils that the porphyrin content increases with the sulfur content of the oil. When they examined crude oils with less than 0.7 percent sulfur, they found very little or no porphyrins present. The sulfur content of the Mississippian crude oil investigated in this work is less than 0.3 percent (table 23). Dunning et al. (1953, 1954) have shown also that the porphyrins are interfacially the most active compounds in crude oil. The lack of these constituents in the Mississippian oil is probably the reason why the interfacial tension measurements revealed very little activity (table 27).

Another significant result of this work is the fact that sediment centrifuged from a mixture of heptane and crude oil has an apparent particle size of about 30 Å (table 22). This is interpreted as indicating that the addition of heptane brings down the sediment that could normally be centrifuged out of the oil, plus a substantial amount of other smaller particles by causing them to flocculate into sizes big enough to be sedimented within the period of centrifugation.

When this heptane-precipitated sediment is mixed in benzene, however, the flocculat-

ed particles are again dispersed to their limiting particle sizes. The resulting sedimentation coefficient will tend to reflect the movement of the smaller particles present, and thus the average of 30 Å is obtained in this case, compared with the 40 Å value determined previously for sediment centrifuged from undiluted oil. (As the larger particles will tend to move faster than the smaller ones, the concentration gradient in the vicinity of the sedimentation boundary will be less and the light-transmission curves should therefore display less slope, which means a more diffuse boundary. A comparison of the curves on figure 19, for the heptane-oil sediment in run No. A-1878, with others for sedimentation in benzene reveals this to be the case.)

The sediment obtained by centrifuging the benzene-oil mixture in run No. A-1879 (fig. 20) was not easily distinguished from the benzene-oil liquid and apparently a mixture of what would normally be sediment plus a small proportion of smaller particles was analyzed. This resulted in a slightly smaller average particle size for the benzene-oil sediment, about 36 Å. For sediment centrifuged from heptane-oil and benzene-oil mixtures, it was necessary to assume a particle density of 1.2 g/cm.³ (table 22). A correct density should be obtained for this material to check the validity of these preliminary interpretations.

The failure to centrifuge any organic sediment out of the California crude oil, is believed due primarily to the extremely high viscosity of this youthful petroleum. There are two possible approaches to the problem of centrifuging this oil. One approach would be to attempt preparative centrifuge runs at elevated temperatures so as to take advantage of the much lower viscosities. This oil has a high asphaltic content (Dunning et al., 1953), and another approach would be to dilute the oil with benzene and centrifuge analytically.

If more quantitative results are desired, the asphaltic content could be precipitated in a series of fractions using appropriate solvents. It is well known that as the lighter paraffin hydrocarbons are added to asphalt

or crude oil, more precipitate is formed. Kalichevsky (1938, p. 82) has suggested that in the presence of such solvents of decreasing molecular weight more substances in the asphalt behave as colloids. On this basis, one should start with the heavier hydrocarbons as the initial precipitating agents in an effort to achieve fractional precipitation of the various suspended particles. Each fraction could then be investigated with the ultracentrifuge, using procedures previously outlined.

The above discussion has concerned the sediment that can be completely segregated from crude oil. It is also possible to obtain some idea of the nature of the black and red particles that were segregated within the crude oil but *not* separated from it. The sediment moved to the bottom of the centrifuge tubes first, so it can be presumed that the black and red particles are smaller and/or less dense than the particles of the sediment. It is suspected that these two groups of particles may fall under the general classification of maltenes, which have been reported to contain deep red resins as well as other dark- and light-colored fractions (Sachanen, 1945, p. 396).

The sedimentation behavior of these particles in the crude oil can be used to obtain an approximation of their sizes. After nine days centrifugation at 30,000 r.p.m., it was determined that the boundary between the red and black particles had moved 70 percent of the length of the centrifuge tube. The fact that this boundary moved only a slight distance after three more days of centrifugation suggests that an equilibrium was being approached. If the oil viscosity and density are again assumed to be 10 cp. and 0.84 g/cm.³, respectively, and nine days is taken as an arbitrary sedimentation time for particles with a density of 1.2 g/cm.³ to move 70 percent of the radial path from 6.3 to 9.4 cm., the calculated size of the black particles is about 40 Å, compared to 70 Å for the sediment. If the particle density is assumed to be 1.0 g/cm.³, the corresponding size would be 60 Å, which gives an indication of the effect of this parameter. A similar approach to the red particles indicates that they are

of the order of 20 to 25 Å, if their density is about 1.0 g/cm³. However, the decreased rate of movement with time of centrifugation suggests that either sedimentation equilibrium was being approached or else the densities of the particles were approaching the density of the medium at that level in the centrifuge tube.

Such calculations as the above give only rough approximations although they do suggest the over-all trend in the variation of size and density for the three different groups of particles. A much better approach would be to isolate each fraction and investigate its sedimentation behavior in media of different density. I believe this can be accomplished by centrifuging crude oil long enough to get the maximum concentration of the particles in certain fractions. These fractions can then be isolated by the previously described freezing technique and the particles precipitated by appropriate solvents in the manner described above. Presumably, the larger black particles would be precipitated first and this would tend to separate them from the red particles. A series of centrifugation runs at successively higher gravitational fields might also accomplish particle fractionation, but this was not possible with the preparative centrifuge used in this investigation because the apparatus was operated at maximum permissible speeds.

The curious color banding noted in some runs in centrifuging mixtures of normal heptane and oil (pls. 4C and 4D) is a phenomenon for which no positive explanation can be offered at this time. It might possibly be related to various groups of aggregated particles present in the crude oil—heptane mixture. One would question, however, why the aggregation caused by the heptane should result in a number of discrete particle sizes when a more random aggregation would be anticipated.

The possibility cannot be excluded that this banding is a reflection of several different groups of particles that are indigenous to the crude oil, but the fact that the phenomenon could not always be reproduced casts serious doubt on this interpretation. The effect might have been connect-ed with the way in which the solutions were handled in the centrifuge tubes and therefore not be a characteristic property of the crude oil. In any event, no satisfactory explanation can be offered at this time, and the banding effects are merely reported here.

It is concluded that, from the physicochemical standpoint, there is unequivocal evidence that organic colloidal particles occur in the three Illinois crude oils studied. On the basis of the detailed studies on the Mississippian oil, there appear to be three groups of particles that differ in their sedimentation behavior. The same three groups probably occur in the other two Illinois crude oils, both of which exhibited evidences of fractionation during short preparative centrifugation runs.

It is significant that the black coloring matter in the Mississippian crude oil could be completely centrifuged out of most of the oil, leaving a distinctly different liquid. The fact that the black sediment obtained is composed of asphaltenes is not surprising, but the important implication is that practically all crude oils contain colloidal-sized particles because asphaltic materials are commonly present in petroleum. Furthermore, on the basis of this work, one can anticipate that crude oils probably contain several groups of colloids. This should be a fertile field for further research with the ultracentrifuge.

Results from the Geologic Standpoint

The different amounts of sediment obtained from the three Illinois crude oils is of interest from a geologic standpoint. The Mississippian oil has the highest amount of sediment, the Pennsylvanian next, and the Devonian least (table 13). The amount of sediment collected thus does not correlate with the geologic age of the reservoir rocks. Differences in the three crude oils are evident also on the basis of trace metal content (table 24). It will be noted that the Devonian oil has a significantly lower amount of nickel and vanadium than the other two oils, which are rather similar in metal content. These variations are interpreted as an indication that the three

oils probably have come from different sources.

If we may accept the thesis that petroleum passes from a youthful asphaltic to a mature paraffinic stage, then we would generally expect to find a decreasing amount of asphaltic materials in crude oils of greater geologic age. Such transformations probably also would be dependent upon the degree of diagenesis to which each petroleum source bed had been subjected. Considering this, the differences observed for the three Illinois oils may be a reflection of their mode of genesis, but the inference of different source materials seems to be a more relevant consideration. It is, of course, not surprising to find such variations in view of the geologic and geographic occurrence of these samples within the Illinois basin, but this is an indication of the usefulness of these data in distinguishing between various crude oils when other considerations might not be so clear cut.

The presence of the inorganic material centrifuged from the various crude oils is a point that may have much geologic significance. The various hexagonal-shaped particles that were noted many times in the electron microscopy work are believed to be clay minerals of the kaolinite group. Reference to any of several recent works on electron microscopy of clay surfaces will reveal that this hexagonal outline is typical of kaolinite (Grim, 1953, ch. 6; Bates and Comer, 1955; Taggart et al., 1955). The lath-shaped particles found in the Mississippian, Devonian, and Californian crude oils may also be clay minerals but this is less certain. It would, of course, be highly desirable to produce a more positive identification by x-ray analysis, but this was not possible with the very minor amounts of material available in this study. Clays have been reported before as occurring in crude oil and are thought to be one of the causes of emulsions (Morrell and Egloff, 1931).

The presence of these clay-like materials raises the question of whether they are remnants of the sediment in which the original petroleum source materials were deposited. As they are of the order of one micron in size, they could very easily be swept along with the crude oil as it migrated from the source bed to the point of entrapment. One possible method of checking this would be to study the suites of clay minerals that could be centrifuged from various crude oils and compare them with the clays of the reservoir rock. Significant differences would indicate that the oil and suspended clay minerals probably came from other sources. This could provide data on the important question of whether or not crude oil forms *in situ*, as several workers have suggested (Levorsen, 1954, p. 510-512; Corbett, 1955).

As the clays may have played an important role in the low-temperature catalytic transformation of petroleum, perhaps some sort of relict structures of the hydrocarbons could be found associated with these clay minerals. For example, Grim (1947) has postulated that a residue of carbon might be left behind on the surface of active clays associated with petroleum. The very intimate mixing of dispersed clay minerals in crude oil would, of course, be the most favorable condition for catalytic cracking. This possibility merits further investigation of crude oils of several geologic ages. On the basis of my brief work on the California oil of Pleistocene age, it would appear that the geologically younger crude oils will contain significantly more inorganic sediment. An investigation of a group of these oils might provide the most fruitful starting point.

Will petroleum genesis be reflected in the colloidal components of petroleum? As has been demonstrated, there are at least three groups of colloidal particles in the Illinois crude oils, ranging from the asphaltenes to what are probably hydrocarbons of the maltene group. As the asphaltic crude oils are believed to represent a youthful stage in petroleum genesis, the low-temperature transformation process apparently reduces the large asphaltic colloids to particles of smaller dimensions and lighter density and eventually to paraffin hydrocarbons. Thus, the material is metamorphosed from a relatively high aromatic type of hydrocarbon to an aliphatic type.

By procedures that have been outlined in this work, it should be possible to isolate the colloidal components from a group of crude oils selected over a wide geologic range. The aliphatic-aromatic nature of these components can be determined, and if the above theory of petroleum genesis holds, we can expect to find a gradual increase in the smaller, more aliphatic colloids at the expense of the original asphaltic particles as geologic age increases. The relative proportions of these various colloidal constituents and their variation with geologic time would be important considerations in this approach to petroleum genesis.

Results from the Standpoint of a New Technique

Centrifugation as employed in this work makes possible the isolation and study of colloidal components in crude oil in a manner that apparently has not been used heretofore. Such a tool will make it possible not only to investigate the general nature of petroleum, with all of the implications in regard to genesis, but perhaps also to isolate the important surface-active constituents of crude oil. For example, investigations on the collodial nature of the porphyrins may provide basic data that will be helpful in the understanding of their high interfacial activity.

The ultracentrifuge also could be used in research on asphalt. Investigations on the various components of asphalt should be of assistance in interpreting the rheological properties, which are important in industrial applications.

The ultracentrifuge thus obviously can be used to great advantage in studying the nature of petroleum and in isolating and characterizing the colloidal components, clearly demonstrated to exist in the crude oils used in this study.

SUMMARY

The question of whether or not colloidal particles exist in crude oil in its natural state has long been a fundamental problem. If such particles are present, they must be intimately involved with the other constituents and, by the very nature of colloidal systems, one would expect the physical and chemical properties of the oil to be influenced significantly. Thus, a knowledge of the possible colloidal components in crude oil would be of great assistance in many fields of research on petroleum.

A search of the literature for evidence on the presence of colloidal particles in petroleum reveals a lack of unequivocal data and often a confusion of conflicting statements. For example, many workers in the past have considered as indications of the colloidal nature of petroleum the waxes that are known to be associated with paraffinic oils, the coagulation of bituminous materials from asphaltic oils, the optical heterogeneity of oil, and the ability of surface-active materials such as fuller's earth to decolorize hydrocarbons. This indirect evidence has not been definite proof, however, because others have shown that waxes exist as microcrystals in petroleum, and the precipitation of asphaltic materials from oil requires large proportions of solvents so that the effect may simply be one of a change in solvent with resultant ordinary precipitation. Furthermore, the light scattered by oil is only weakly polarized, and therefore the reported optical effects are probably due to the well known fluorescence of petroleum rather than to scattering by dispersed particles.

Attempts have also been made to prove the existence of colloids in petroleum, and in asphalts as well, by ultrafiltration and by direct examination with the ultramicroscope and with the electron microscope. Although these investigations have been unsuccessful in finding dispersed particles, they have at least indicated that if colloidal particles do exist in crude oil or asphalt they must be quite small—something less than 65 Å.

Whereas the properties generally characteristic of the colloidal state are only very indefinitely developed in petroleum, investigators of asphalt seem to have no doubt that they are dealing with a colloidal system. Extensive studies of the rheological properties of asphalt have led to this conclusion and to the division of asphalt into two general categories: maltenes, which is that

portion that is soluble in aromatic-free gasoline or diethyl ether, and asphaltenes, the insoluble portion.

The general concept of this colloidal system is that the asphaltenes are the centers of micelles with the maltenes adsorbed on the surfaces of the asphaltene particles. The structure of the micelle is postulated as having as a nucleus the substances of the greatest molecular weight and with the most pronounced aromatic nature. Around this nucleus are arranged lighter and less aromatic constituents, and there is a gradual transition to more or less preponderantly aliphatic compounds. In other words, there is no distinct interface within the micelle or between it and the surrounding environment.

If asphalt is accepted as a colloid system, one is inclined to suspect that petroleum should be too. For example, the asphaltic materials separated from crude oil have distinct colloidal properties, and it seems improbable that precipitation of these materials by hydrocarbon solvents should produce any chemical change in the substance precipitated. On the other hand, very careful electron microscopy has failed to find discrete particles in either crude oil or in asphalt. Perhaps the postulated micelle concept mentioned above provides an explanation. If there is no definite interface between the micelle and its environment, then any dispersed particles that may exist in petroleum do not provide a reflecting surface to beams of light or electrons.

One approach to the solution of this problem, apparently never attempted, is the use of the ultracentrifuge to impose a gravitational field sufficient to cause any particles of colloidal dimensions to be separated from their environment. If the asphaltenes exist in petroleum as colloids, they should be affected by such centrifugal forces because their specific gravity exceeds 1.0, whereas most crude oil gravities range from 0.8 to 0.95. The chief purpose of this research has been to explore this idea and to present some rather limited results to demonstrate the usefulness of the method.

Extensive studies have been carried out on one Mississippian oil from the Illinois basin, and additional work has been done on Devonian and Pennsylvanian samples from the same basin in an effort to develop geologic correlations. A California crude oil of Pleistocene age, having physical properties significantly different from the Illinois oils, also has been studied briefly.

Centrifugation of the Illinois crude oils for two to four days at 30,000 r.p.m. produces measurable amounts of a black, tarry, organic sediment. After 53 hours at 30,000 r.p.m., the weight percent sediment for the Mississippian oil was 1.1; for the Pennsylvanian oil 0.4; and for the Devonian oil, about 0.2. Thus, the amount of sediment collected does not correlate with the geologic age of the reservoir rocks. From the standpoint of the nickel and vanadium content, which are the predominant trace metals in these three crude oils, the Mississippian sample has 2.2 ppm Ni and 1.0 ppm V; the Pennsylvanian sample has 2.4 ppm Ni and 1.7 ppm V; while the Devonian sample has only 0.69 ppm Ni and 0.37 ppm V. These variations in amount of sediment and trace metal content of the oil are interpreted as an indication that these three oils probably have come from different sources. The geologic and geographic sources of these three samples within the Illinois basin supports this contention.

Trace metal determinations on the sediment centrifuged from the Mississippian crude oil revealed that the nickel and vanadium are 20-30 times more concentrated in the sediment than in the crude oil, indicating that some kind of metal-organic complexes probably are involved. No metal porphyrins were found in either the Mississippian sediment or its ethyl alcohol extract. Investigations on a large number of Russian crude oils have revealed that little or no porphyrins were found when the sulfur content of the oil was less than 0.7 percent (Radchenko and Sheshina, 1955), and the Mississippian crude oil has less than 0.3 percent sulfur.

Organic particles of colloidal dimensions were segregated from the Illinois crude oils because their size and density were sufficiently greater than that of the media in which they were dispersed. Prolonged cen-

trifugation experiments on the Mississippian crude oil have further demonstrated that there are at least three general groups of discrete particles dispersed in the oil: one group that can be centrifuged completely out of suspension, which is the above-mentioned *sediment;* a second group that apparently contains the remaining black coloring matter in the oil and can almost be removed from suspension at 30,000 r.p.m. and which is referred to as *black particles,* and a third group that contains other pigmented particles that in transmitted light have a distinct reddish color and are referred to as *red particles.* As considerable fluorescent matter remained in the supernatant liquid, it would not be surprising to find other groups of particles by application of higher gravitational fields, and this point merits further study.

The organic sediment centrifuged from the Mississippian crude oil falls under the broad classification of asphaltenes. Elemental analyses gave a C/H ratio of 0.91, and x-ray analysis indicated a ratio of the intensities of the 4.5 Å to 3.5 Å reflections of about 0.9. Both criteria are typical of the asphaltenes, which are a complicated mixture of aliphatic chains and aromatic ring structures. Infrared absorption spectra corroborated the aliphatic-aromatic nature of this material and indicated that partly oxidized structures also are involved. The solubility characteristics and general appearance of the sediment gave further support to the asphaltene classification. The sediment centrifuged from the Devonian and Pennsylvanian crude oils has been given the same classification on the basis of several similarities with the Mississippian sediment.

The asphaltenes centrifuged from the Mississippian crude oil were further investigated by determining their sedimentation coefficients in benzene, carbon tetrachloride, and mixtures of the two, using analytical centrifugation procedures. After the experimental data were referred to a common reference state, which involved several important corrections including the effects of compressibility, an excellent linear correlation of sedimentation coefficient versus density of dispersing medium was obtained. This indicated that the various media used had no effect on the size, shape, or density of the dispersed asphaltene particles.

By interpolation of these data, a density of 1.22 g/cm.³ was obtained for sediment centrifuged from crude oil that had been collected under a nitrogen atmosphere. A similar correlation for sediment from Mississippian oil collected in air gave a density of 1.26 g/cm.³, but further work is needed to establish the indicated difference. These values are true densities, if the density of any solvated material is the same as that of the dispersing agent. Since the above correlations indicate that the dispersed particles were unaffected by the various media in which they were investigated, it is inferred that the degree of solvation of these asphaltene particles was not an appreciable factor. This is an important point that needs to be investigated further.

Once a particle density is established, it is possible to calculate particle size and molecular weight if the shape is known. From rheological studies of the asphalts, several workers have postulated spherical shapes for the asphaltene micelle. Electron micrographs of this material at 100,000 magnifications also suggest round shapes. Others have assumed a linear shape for asphaltene particles, but such a configuration has not been demonstrated. It was therefore concluded that a spherical shape was a reasonable assumption to adopt, and on this basis the Mississippian sediment was categorized as being asphaltene particles of about 40 Å in diameter having a density of 1.22 g/cm.³ and a molecular weight of 30,000. Similar results were obtained with the Pennsylvanian and Devonian crudes, and this suggests that 40 Å is an average unit particle dimension for the asphaltenes.

As the asphaltenes seem to have a fixed 40 Å size when dispersed in benzene or carbon tetrachloride, it is postulated that the unit dimension of these particles in petroleum is approximately the same. This seems to be confirmed by approximate calculations, which give about 70 Å diameter and are based on the distance traveled by the sediment in prolonged centrifuge experi-

ments. An electron micrograph of the sediment obtained from the Mississippian oil reveals many particles of the order of 50 Å in diameter, although some degree of aggregation may have resulted from the method of preparing the sample. These results are in agreement with literature values of 85 Å for the asphaltenes, as determined from x-ray data, and something less than 65 Å, as inferred from electron microscopy work.

The molecular weight of 30,000 obtained in this work falls between the lowest and highest values, 1,000 and 140,000, respectively, available in the literature. The various methods by which these latter results were obtained, however, cast some doubt on their reliability. Until the degree of homogeneity of asphaltenes from a variety of sources has been defined, it seems quite possible that there may be a significant range in the molecular weights of such materials. The ultracentrifuge could be used very effectively in evaluating this fundamental property of the asphaltenes.

Some idea of the nature of the black and red particles, which probably are maltenes and were segregated within the oil but *not* separated from it, may be deduced from the distances these particles traveled in the prolonged centrifuge experiments. Assuming a density of 1.2 g/cm.³ for the black material, the calculated average particle size is about 40 Å, compared to 70 Å for the sediment. A similar approach to the red particles indicates they are of the order of 20-25 Å, if their density is about 1.0 g/cm³. At best such calculations can give only rough approximations, but they do indicate the overall trend in the variation of size and density for the three categories of colloidal particles. A much better approach would be to isolate each fraction and investigate its sedimentation behavior by procedures that are briefly outlined.

The occurrence of asphaltenes in the black sediment that was centrifuged from the Mississippian oil is consistent with the fact that Illinois crude oils are generally somewhat asphaltic. Thus, it is not surprising that the other two Illinois oils investigated also contain asphaltenes. The important implication is, however, that practically all crude oils contain colloidal-sized particles because asphaltic materials are commonly present in petroleum. Furthermore, on the basis of this work one can anticipate that crude oils probably will contain several groups of colloidal particles. This should be a fertile field for further research with the ultracentrifuge.

In addition to the organic sediment that was centrifuged from the Illinois crude oils, a very minor amount of an inorganic sediment also was obtained. Electron micrographs of this material revealed a significant amount of hexagonal-shaped particles that are believed to be kaolinite platelets. Lath-shaped particles also were observed that may be clay minerals, but this is less certain. Although no organic sediment could be centrifuged from the California crude oil because of its extremely high viscosity, significantly more inorganic sediment was obtained than for the Illinois oils, and in it a substantial amount of lath-shaped particles was observed.

It is postulated that any clay minerals suspended in the oil may possibly be related to the original source beds from which the petroleum migrated to its point of entrapment. It would be informative, therefore, to identify the clays that can be centrifuged from crude oil and compare them with the clay minerals of the reservoir rock to determine whether petroleum is formed *in situ*, as others have suggested. As the clays may have played an important role in the low-temperature catalytic transformation of petroleum, there is a possibility that some sort of relict structures may exist on the clay surfaces that would shed some light on petroleum genesis.

Another possible approach to petroleum genesis may be an evaluation of the relative proportions of the various groups of colloids in crude oil. As petroleum is believed by some workers to be metamorphosed from a youthful asphaltic stage to a mature paraffin stage, one should anticipate a transformation of large asphaltic colloids to particles of smaller dimensions and lighter density and eventually to paraffin hydrocarbons. By procedures that have

been outlined in this work, it should be possible to isolate the various colloidal components from a group of crude oils that have been selected over a wide geologic range. The aliphatic-aromatic nature of these components can be determined, and if the above theory of genesis holds, there should be a gradual increase in the smaller, more aliphatic colloids at the expense of the original asphaltic particles as geologic age increases. Perhaps information such as this will shed new light on the mode of origin of petroleum.

Centrifugation as employed in this work makes possible the isolation and study of colloidal components in crude oil by a method that heretofore has apparently not been used. With this approach it has been possible to obtain unequivocal evidence of the existence of organic colloidal particles in the three Illinois crude oils studied. It is concluded that the ultracentrifuge can be used to great advantage, not only to investigate the general nature of petroleum, with all of the implications in regard to genesis and exploitation, but also in other fields of research on hydrocarbons where a knowledge of colloidal behavior is important.

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APPENDICES

A.—PROCEDURE FOR COLLECTING CRUDE OIL UNDER NITROGEN

Details of the procedure for collecting crude oil samples under an atmosphere of nitrogen are as follows. The numbers mentioned below refer to stopcocks or valves shown diagrammatically in figure 29.

1. After all glassware had been cleaned, the assembled apparatus was evacuated, through No. 3 to approximately 1 mm. Hg. absolute pressure, filled with nitrogen to atmospheric pressure, re-evacuated, and filled a second time with nitrogen until the manometer indicated about 3 cm. Hg. positive pressure. The apparatus was then taken to the field and connected to the wellhead as shown in figure 29.

2. After the nitrogen bottle was connected, the rubber tubing was purged for about five minutes through No. 4. No. 2 was opened to check the pressure inside the separatory funnel, and the apparatus was not used unless a positive pressure still existed, which would indicate that air had not entered the system. With a positive pressure indicated, No. 4 was opened, and a slight flow of nitrogen was established through vent while maintaining about 3 cm. Hg. positive pressure. This vent flow was maintained throughout the sampling operation.

3. The rubber tubing to the wellhead was next purged for about five minutes with nitrogen by opening No. 3 and the two ¼-inch valves, 5 and 6, on the manifold, keeping No. 7 shut. Flow rates were regulated so that manometer showed about 3 cm. Hg. positive pressure continuously. After the purging, No. 5 was shut, and the manifold was purged with well fluids when valve 7 was opened to permit outflow through valve 6.

4. With well fluids flowing out through No. 6, valve 5 was opened slowly and the nitrogen source regulated as necessary to maintain about 3 cm. Hg. positive pressure at manometer. With No. 4 still open, No. 6 was partially closed until pressures were sufficient to divert part of the oil and water over to the sampling apparatus. In this way, the vent served to discharge any natural gas, released from solution in the oil, as well as the displaced nitrogen. Slight surging conditions in the producing well also were offset by keeping No. 6 partially open.

5. Any water that accumulated in the separatory funnel was drained off through No. 1, and the procedure was continued until an adequate sample of crude oil was obtained. After sampling was completed, the system was automatically at a positive pressure of about 3 cm. Hg. and was shut off at this pressure for transfer to the laboratory. The separatory funnel was checked periodically en route to the laboratory to relieve excessive pressures caused by the release of solution gas, which can be especially troublesome on hot days. In the relatively constant temperature of the laboratory, positive pressures were easily maintained.
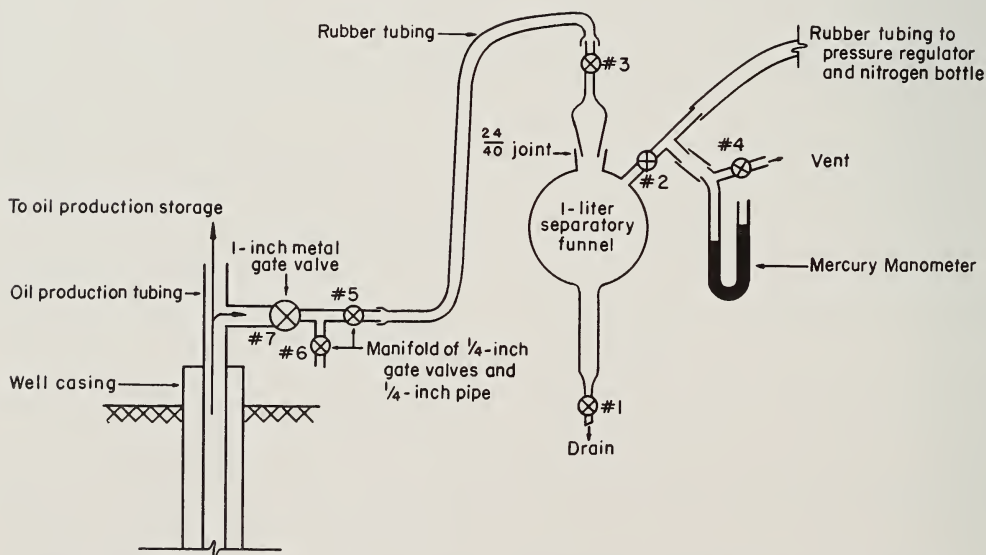

Fig 29.—Apparatus used to collect crude oil under nitrogen atmosphere at producing well.

B.—PROCEDURE FOR FILLING PREPARATIVE CENTRIFUGE TUBES UNDER NITROGEN

Details of the procedure for filling the preparative centrifuge tubes under an atmosphere of nitrogen are as follows. The numbers mentioned below refer to stopcocks or valves shown diagrammatically in figure 30.

1. With a positive pressure of about 3 cm. Hg. inside the separatory funnel and No. 2 open, the ground glass joint at the top of the funnel (see fig. 29) was loosened slightly to allow a flow of nitrogen out the top. Pressures were regulated during this and all subsequent operations so that the manometer remained close to 3 cm. Hg. positive pressure.

2. When a flow of nitrogen out the top of the funnel had been achieved, the ground glass joint was replaced by the glass and Tygon tubing arrangements shown in figure 30. This arrangement was first purged with nitrogen before the rubber stopper was set.

3. Several centrifuge tubes were then placed in a holder inside the large glass beaker, and screw clamp 4 was opened until a substantial flow of nitrogen into the bottom of the beaker was established.

4. After the glass beaker had been purged for perhaps 20 minutes, each individual centrifuge tube was further purged by insertion of the rubber tubing to the bottom of each tube.

5. The Tygon tubing was filled with crude oil through No. 3, and any excess oil was caught in the bottom of the beaker.

6. The centrifuge tubes were then filled with oil and the metal cap for each tube was put in place while the tube was still inside the beaker. A substantial flow of nitrogen through the purge line into the bottom of the glass beaker was maintained throughout the filling operations.

7. After the caps were in place, the tubes were removed, the caps tightened, and the samples were ready to be centrifuged.

C.—DERIVATION OF FORMULA FOR CALCULATING PRESSURE IN CENTRIFUGING SOLUTIONS

We shall assume that the concentrations of the solution being centrifuged are low enough so that movement of any dispersed particles does not appreciably affect the liquid density. We shall also assume that there is a linear relationship between density of the solvent and pressure up to the maximum anticipated pressure of this system.

On this basis, an incremental pressure increase at any point in the liquid is dependent upon the effective density at that point and the acceleration of the centrifugal field, or

$$dP = d_{mx} w^2 x \, dx \qquad (20)$$

where

$dP =$ pressure increment
$d_{mx} =$ effective density of liquid at x
$w =$ speed of rotation
$x =$ distance from center of rotation
$dx =$ incremental distance across which dP occurs

As a linear relationship between density and pressure is assumed, we can write

$$d_{mx} = mP_x + d_i \qquad (21)$$

where

$m =$ slope of the variation between density and pressure
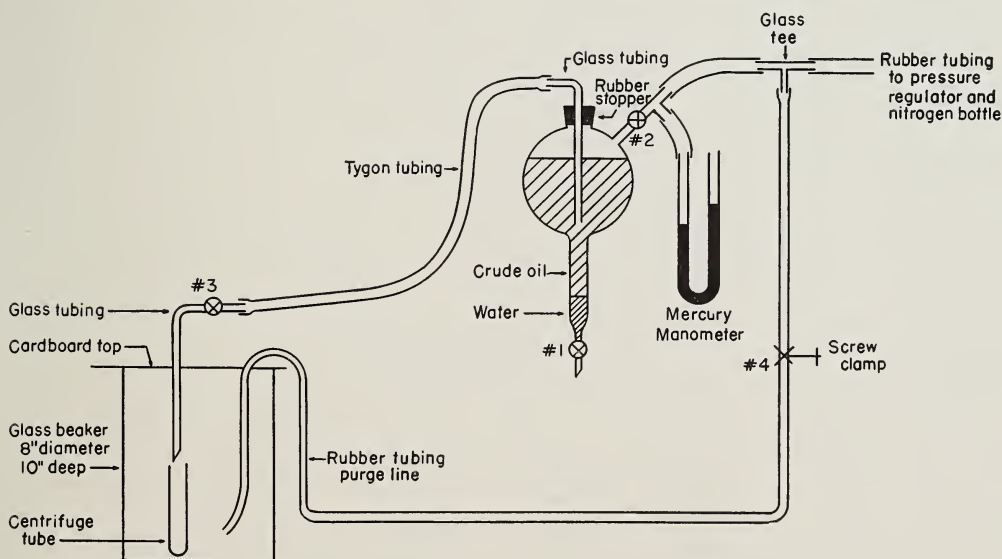$P_x =$ pressure at any point, x
$d_i =$ density of solvent at meniscus

Fig. 30.—Apparatus used to fill centrifuge tubes under nitrogen atmosphere.

By combining equations 20 and 21, we obtain

$$dP = (mP_x + d_i) w^2 x \, dx \qquad (22)$$

Separating the variables and integrating equation 22 between the limits $P = 0$, $x = x_i$, and $P = P_x$, $x = x$, where x_i is the distance to the meniscus, yields

$$\frac{1}{m} \ln \left(\frac{mP_x + d_i}{d_i} \right) = \frac{w^2 (x^2 - x_i^2)}{2} \qquad (23)$$

Equation 23 can be rearranged to the form

$$P_x = \frac{d_i}{m} \left(e^{\frac{mw^2(x^2 - x_i^2)}{2}} - 1 \right) \qquad (24)$$

If P_x is expressed in atmospheres (above atmospheric) and cgs units are used elsewhere, equation 24 is modified to

$$P_x = \frac{d_i}{m} \left(e^{\frac{mw^2(x^2 - x_i^2)}{2.026 \cdot 10^6}} - 1 \right) \qquad (25)$$

D.—DENSITY OF BENZENE AS A FUNCTION OF PRESSURE AT 23°C

To obtain densities of benzene at atmospheric pressure, the following formula from the International Critical Tables (1928, v. 3, p. 29) can be used.

Density, $g/cm^3 = 0.90005 - 1.0636 \cdot 10^{-3} t - 0.0376 \cdot 10^{-6} t^2 - 2.213 \cdot 10^{-9} t^3$, where $t = °C$.

Michaels (1948) has included data on the density of benzene as a function of pressure in his doctorate thesis for 50° and 95°C, which data are available in the literature (Bridgman, 1931, p. 210). Bridgman also provided him with data for 20°, 40°, 60°, 80°, and 100°C, that apparently are not available in the literature. These data are summarized below.

In correlating these data, Michaels (1948, fig. 23) provides a graph of the density of benzene as a function of pressure for various temperatures, from which the following data were read directly.

The above data are plotted in figure 31, and it will be noted that linear relationships exist up to 500 atm. for all temperatures shown. Such is not the case, however, above 500 atm., as a plot of the more complete data will reveal.

Pressure atm.	Density—g/cm³			
	20°C	40°C	50°C	60°C
10	0.8790	0.8583	0.8475	0.8361
100	0.8850	0.8648	0.8548	0.8444
200	0.8916	0.8720	0.8627	0.8534
300	0.8982	0.8794	0.8706	0.8625
400	0.9049	0.8869	0.8786	0.8715
500	0.9115	0.8940	0.8868	0.8805

By crossplotting the above data and extrapolating to 23°C, the density-pressure curve for this temperature was obtained as indicated. The density of benzene at 1 atm. and 23°C, as calculated from the
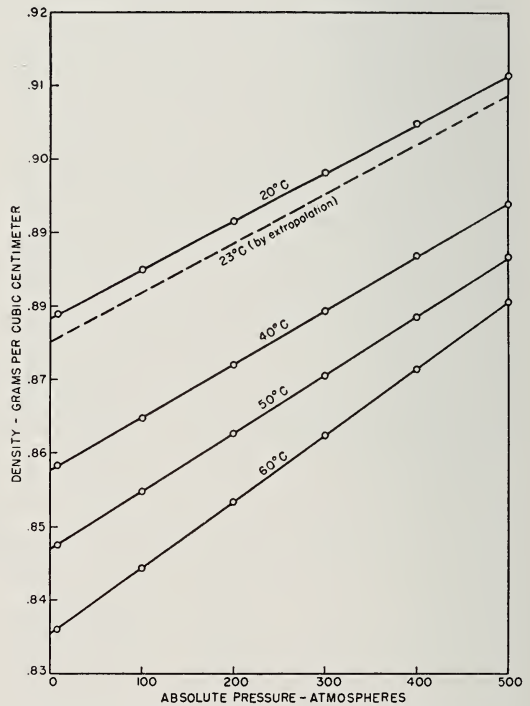

FIG. 31.—Density of benzene as a function of pressure for various temperatures.

Pressure Kg/cm²	Density ratio, d$_o$/d*						
	20°C	40°C	50°C	60°C	80°C	95°C	100°C
0	1.0246	1.0498	1.0630	1.0772	1.1066	1.1295	—
500	0.9862	1.0048	1.0160	1.0190	1.0444	—	1.0651
1000	—	0.9751	0.9841	0.9862	1.0072	1.0201	1.0241
1500	—	0.9513	0.9591	0.9610	0.9796	0.9916	0.9949

*Reference d_o = 0.90005 g/cm³ at 0°C.

above mentioned formula from the International Critical Tables, is 0.87554, which compares with 0.8752 read from figure 31.

The equation of the 23°C isotherm on figure 31 was calculated to be

$$d_{mx} = 6.714 \cdot 10^{-5} \, P_x + 0.8752$$

where

d_{mx} = density of benzene at pressure P_x, g/cm³

P_x = pressure (above atmospheric), atm.

E.—VISCOSITY OF BENZENE AS A FUNCTION OF PRESSURE AT 23°C

To obtain viscosities of benzene at atmosphere pressure, the following formula from the International Critical Tables (1929, v. 5, p. 12) can be used.

$$\text{Viscosity, poise} = \frac{14.42}{(90 + t)1.64}$$

where t = °C

Bridgman (1926, p. 80) has published the following data on the viscosity of benzene as a function of pressure at 30°C and 75°C.

		Pressure — Kg/cm²		
		1	500	1000
Log v/v₃₀	30°C	0.000	0.173	0.347
Log v/v₃₀	75°C	−0.235	−0.062	0.081

where v_{30} = 0.00566 poise

It is evident that the change in the log function is 0.173 up to 500 kg/cm² for either temperature, and therefore it can be assumed that this will also hold at 23°C. Bridgman (1926) further states that the relationship between log v/v₃₀ and pressure is essentially linear to 500 kg/cm². Therefore, we can assume the same thing for log v_x/v_{23}, and thus

$$\text{Log} \frac{v_x}{v_{23}} = \frac{0.173 \, P_x}{500 \, (.9678)} = 0.3575 \cdot 10^{-3} P_x$$

Using the above mentioned formula from the International Critical Tables, v_{23} at 1 atm. is 0.00622 poise and therefore:

$$\text{Log} \frac{v_x}{0.00622} = 0.3575 \cdot 10^{-3} \, P_x$$

where

v_x = viscosity of benzene at pressure P_x, poise

P_x = pressure (above atmospheric), atm.

F.—INTEGRATION OF F(X) BY NUMERICAL METHODS

The function $\dfrac{v_x}{(d - d_{mx})x}$ can be evaluated at selected values of x as shown in the table below. Here benzene is used as the example. A plot of f(x) versus x is shown in figure 32, and because of the small amount of curvature, the area under the curve between any two points may be determined quickly by applying the trapezoidal rule. This area is, of course, the desired integral and the calculations are summarized below.

x	$v_x \cdot 10^{3}$*	d_{mx}*	$d - d_{mx}$†	f(x)‡	Average f(x)‡	x $\int f(x)dx$** 5.9
5.9	6.22	0.8752	0.3748	0.002813		0
					0.002817	
6.0	6.32	0.8765	0.3735	0.002820		0.0002817
					0.002826	
6.1	6.43	0.8779	0.3721	0.002833		0.0005643
					0.002840	
6.2	6.54	0.8793	0.3707	0.002846		0.0008483
					0.002852	
6.3	6.65	0.8807	0.3693	0.002858		0.0011335
					0.002868	
6.4	6.78	0.8822	0.3678	0.002879		0 0014203
					0.002888	
6.5	6.90	0.8836	0.3664	0.002897		0.0017091
					0.002909	
6.6	7.03	0.8852	0.3648	0.002920		0.0020000

* Assumed conditions: 59,750 r.p.m. and t = 23°C.

† d = 1.25 g/cm³.

‡ $f(x) = \dfrac{v_x}{(d - d_{mx})x}$
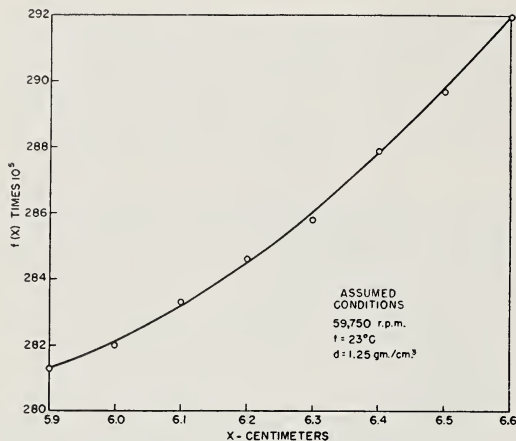
**Δ x = 0.1 cm for each value of x.

Fig. 32.—F (x) versus x for sedimentation in benzene.

G.—DENSITY OF CARBON TETRACHLORIDE AS A FUNCTION OF PRESSURE AT 23°C

To obtain densities of carbon tetrachloride at atmospheric pressure, the following formula from the International Critical Tables (1928, v. 3, p. 28) can be used.

Density, $g/cm^3 = 1.63255 - 1.911 \cdot 10^{-3} t - 0.690 \cdot 10^{-6} t^2$

where   t = °C.

Bridgman (1931, p. 212) gives the following compressibility data for carbon tetrachloride.

Pressure kg/cm²	Density ratio, d_o/d*	
	50°C	95°C
0	1.0000	—
500	0.9519	0.9928
1000	0.9192	0.9540

*d_o=1.5353 g/cm³ at 50°C.

Other compressibility data for 20°C and 24.6°C were obtained in the International Critical Tables (1927, v. 2, p. 35) and are listed below.

From these two sets of data, densities at 20°, 24.6°, and 50°C were calculated and the results are shown graphically on figure 33. Straight lines have been drawn for all three temperatures, and although some deviations occur at 20° and 24.6°C, the maximum difference of the data from the straight line is less than 0.2 percent.

By crossplotting data from the straight lines and extrapolating to 23°C, the density-pressure curve for this temperature was obtained as indicated. The density of carbon tetrachloride at 1 atm. and 23°C as calculated from the above mentioned formula from the International Critical Tables is 1.5882,

t	Pressure Megabaryes	B*	t	Pressure Megabaryes	B*
20°C	1–100	90	24.6°C	29.4	99
	100–200	88		98.1	93
	200–300	82		196.2	86
	300–400	74		294.3	79
	400–500	69		392.4	73
				490.5	67
				588.6	62

*$B = \dfrac{10^6 (V_1 - V_2)}{V_1 (P_2 - P_1)}$ where V = volume, any units and P = pressure, megabaryes

which was used in deriving the following equation for the 23°C isotherm.

$$d_{mx} = 1.3788 \cdot 10^{-4} P_x + 1.5882$$

where

d_{mx} = density of carbon tetrachloride at pressure P_x, g/cm³
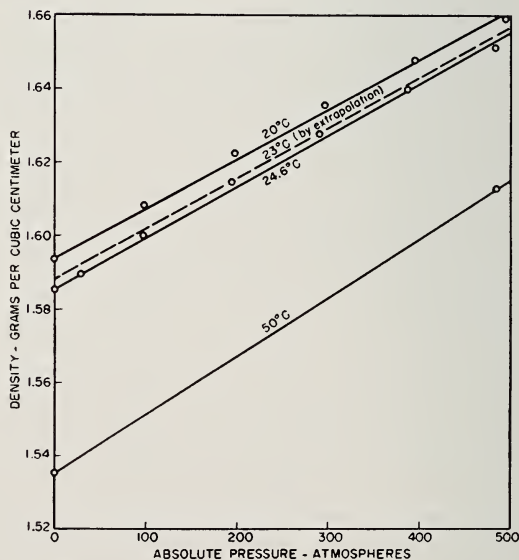
P_x = pressure (above atmospheric), atm.

Fig. 33.—Density of carbon tetrachloride as a function of pressure for various temperatures.

H.—VISCOSITY OF CARBON TETRACHLORIDE AS A FUNCTION OF PRESSURE AT 23°C

Data on the atmospheric viscosity of carbon tetrachloride were taken from the International Critical Tables (1929, v. 7, p. 212) as follows.

t°C	v cp.
14.89	1.0476
21.21	0.9517
27.56	0.8705
35.21	0.7855
42.08	0.7198

A plot of these data is shown in figure 34 from which the viscosity at 23°C was read as 0.00928 poise.
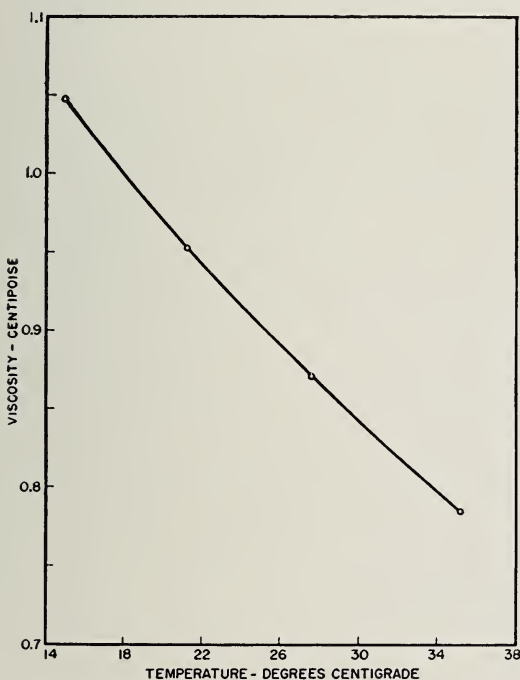

FIG. 34.—Viscosity of carbon tetrachloride as a function of temperature at 1 atmosphere.

Bridgman (1926, p. 79) has published the following data on the viscosity of carbon tetrachloride as a function of pressure at 30°C and 75°C.

	Temp. °C	Pressure—kg/cm²		
		1	500	1000
Log v/v₃₀	30	0.000	0.190	0.351
Log v/v₃₀	75	−0.240	−0.051	0.100

As the change in the log function is 0.190 at 30°C and 0.189 at 75°C up to 500 kg/cm², it was assumed that this function would change by 0.190 at 23°C.

As in the case of benzene, Bridgman (1926) indicates an almost linear relationship between log v/v_{30} and pressure up to 500 kg/cm². Therefore, the formula used was

$$\log \frac{v_x}{v_{23}} = \frac{0.190\, P_x}{500\,(.9678)} = 0.3926 \cdot 10^{-3}\, P_x$$

or substituting 0.00928 for v_{23}, the equation becomes

$$\log \frac{v_x}{0.00928} = 0.3926 \cdot 10^{-3}\, P_x$$

where v_x = viscosity of carbon tetrachloride at pressure P_x, poise

P_x = pressure (above atmospheric), atm.

I.—DENSITY AND VISCOSITY OF 2:1 MIXTURE OF BENZENE AND CARBON TETRACHLORIDE AT 23°C

The density of this mixture was measured, using a Westphal balance with the following results: 1.1150 g/cm³ at 21.8°C; 1.1109 at 25.0°C; and 1.1049 at 29.2°C. By extrapolation of these data, d=1.1135 g/cm³ at 23°C.

From Appendix D, the variation of density with pressure for benzene is 6.714 · 10⁻⁵ g/cm³ atm. at 23°C and from Appendix G, the same value for carbon tetrachloride is 1.3788 · 10⁻⁴ g/cm³ atm. It seems reasonable that for any mixture of these two solvents, this factor should be intermediate between these limits and the linear proportionality assumed was

$$m = \tfrac{2}{3}\,(0.6714 \cdot 10^{-4}) + \tfrac{1}{3}\,(1.3788 \cdot 10^{-4})$$
$$m = 0.9072 \cdot 10^{-4}\ \text{g/cm}^3\ \text{atm.}$$

On this basis, the equation for the density-pressure relationship is as follows:

$$d_{mx} = 0.9072 \cdot 10^{-4}\, P_x + 1.1135$$

where

d_{mx} = density of mixture at pressure P_x, g/cm³

P_x = pressure (above atmospheric), atm.

The viscosity of this mixture was measured with an Ostwald viscosimeter using the ASTM 971-50 procedure with the following results: 0.6619 centistokes at 20.0°C; 0.6169 at 25.0°C; and 0.5852 at 30°C. By extrapolation of these data, v = 0.6331 centistokes or 0.705 centipoise at 23°C.

From Appendix E, the change in log v/v_{30} with pressure up to 500 kg/cm² is 0.173 for benzene and from Appendix H, the change in this same function is 0.190 for carbon tetrachloride at 23°C. Therefore, the following linear proportionality was assumed.

$$\log \frac{v_x}{v_{23}} = \frac{\tfrac{2}{3}\,(0.173) + \tfrac{1}{3}\,(0.190)}{500\,(.9678)}\, P_x$$

or

$$\log \frac{v_x}{0.00705} = 0.3691 \cdot 10^{-3}\, P_x$$

where v_x = viscosity of mixture at pressure P_x, poise

J.—DENSITY AND VISCOSITY OF 1:2 MIXTURE OF BENZENE AND CARBON TETRACHLORIDE AT 23°C

The density of this mixture was measured using a Westphal balance with the following results: 1.3549 g/cm³ at 20.4°C; 1.3482 at 25.0°C; and 1.3415 at 29.1°C. By extrapolation of these data, $d = 1.3510$ g/cm³ at 23°C.

On the basis given in Appendix I for the 2:1 mixture of benzene and carbon tetrachloride, the following linear proportionality was assumed.

$$m = \tfrac{1}{3} \; (0.6714 \cdot 10^{-4}) + \tfrac{2}{3} \; (1.3788 \cdot 10^{-4})$$
$$m = 1.143 \cdot 10^{-4} \text{ g/cm}^3 \text{ atm.}$$

On this basis, the equation for the density-pressure relationship is

$$d_{mx} = 1.143 \cdot 10^{-4} \, P_x + 1.3510$$

where

$d_{mx} =$ density of mixture at pressure P_x, g/cm³

$P_x =$ pressure (above atmospheric), atm.

The viscosity of this mixture was measured with an Ostwald viscosimeter using the **ASTM 971-50** procedure with the following results: 0.6250 centistokes at 20°C; 0.5817 at 25°C; and 0.5466 at 30°C. By extrapolation of these data, $v = 0.5973$ centistokes or 0.807 centipoise at 23°C.

On the basis given in Appendix I the following linear proportionality was assumed:

$$\log \frac{v_x}{v_{23}} = \frac{\tfrac{1}{3} \, (0.173) + \tfrac{2}{3} \, (0.190)}{500 \, (.9678)} \, P_x$$

or

$$\log \frac{v_x}{0.00807} = 0.3809 \cdot 10^{-3} \, P_x$$

where $v_x =$ viscosity of mixture at pressure P_x, poise.