Nature of Colloidal Materials in Petroleum

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THE PRESENCE of colloidal particles in petroleum has been established by Ray, Witherspoon, and Grim (*8*) who studied ultracentrifugation sediments and showed by elemental analysis that they were asphaltene in character.

Most of the ultracentrifugation work on petroleum to date has centered on examinations of actual sediments produced. However, particles remaining in the supernatant liquid were suspected (*7*). This is logical since the amount of sediment obtained from an oil normally is small. Furthermore, the actual sediment may contain extraneous solids common to crude petroleum. For these reasons, emphasis has been placed on the colloidal particles not actually sedimented, but rather, concentrated by centrifugation. Such emphasis is important for oils that are more viscous than those studied by Ray and others (*8*); in oils of medium or high viscosity, very little sediment is obtained. Hence, the properties of colloids still in suspension are of paramount importance.

The physical properties of the colloidal particles of petroleum have been described (*2*). The chemical properties of these colloids were investigated in this study.

EXPERIMENTAL

Centrifugations were carried out in a Spinco Model L preparative centrifuge with a No. 40 angle-head rotor. Most of the studies were performed at a speed of 35,000 r.p.m. which develops an average force of 80,000 times gravity. The range in centrifugal force from the top to the bottom of the tube was from 28 to 81 × 10^3 times gravity. Ultracentrifuge fractions normally were obtained by carefully withdrawing oil from the tube by a hypodermic syringe held in a device so that the tip of the needle followed the meniscus as the tube was emptied. The quantity of sediment rejected to the bottom of the tube was so small that neither measuring nor analyzing it was feasible.

Asphaltenes content was determined by a standardized precipitation with light naphtha. Metals were determined by an x-ray spectrographic method, nitrogen by Kjeldahl method, and sulfur by the Dietert method.

RESULTS AND DISCUSSION

Asphaltenes and Nonhydrocarbons are Colloidal. A sample of Bachaquero crude oil, topped to remove highly volatile components (specific gravity at 60°/60°, 0.974), and diluted with 50% benzene by volume was centrifuged for 70 hours at 80,000 times gravity. The chemical composition of three samples was determined by deasphalting the fractions with light naphtha (C_6 boiling range) and measuring the asphaltenes content. The deasphalted oil was then percolated over alumina and eluted with hexane followed by benzene and pyridine to determine the paraffins, aromatics, and nonhydrocarbons content, respectively. The deasphalting and chromatography were carried out after evaporating the benzene added prior to ultracentrifugation. The results of this study are illustrated in Figure 1.

The increased concentration of asphaltenes and nonhydrocarbons (molecules containing atoms other than hydrogen and carbon) indicates that the colloidal particles are mainly asphaltenes and rich in hetero atoms such as nitrogen, sulfur, or oxygen. The relative constancy of "saturates" concentration down the tube was rather unexpected and apparently is attributable to the broad range of saturates present in petroleum. The nonhydrocarbon portion and asphaltene portion probably are relatively rich in aromatic rings, hence the decrease in "aromatics" toward the bottom of the tube.

Oils other than Bachaquero crude were centrifuged without dilution. These were mostly oils of medium or low viscosity.

In Most Crudes Metals are Associated with Colloidal Asphaltenes. The asphaltenes, vanadium, nickel, and nitrogen contents of the top, middle, and bottom fractions from ultracentrifugation were determined. The results with whole oils are summarized in Table I.

Colloidal materials, which have densities greater than the density of the medium, moved toward the bottom of the tube during ultracentrifugation. As shown from the data, these colloids are rich in asphaltenes, vanadium, nickel, and nitrogen. Furthermore, the vanadium and nickel tend to vary linearly with asphaltenes concentration.

In the Absence of Asphaltenes Little Separation is Observed. In an attempt to determine how closely the colloidal particles of petroleum correspond to asphaltenes, a propane deasphalted raffinate of Tatums (Okla.) crude oil, was ultracentrifuged for 50 hours at an average value of 80,000 times gravity. No significant separation of colloidal asphaltene materials was observed, although the raffinate was much less viscous than the original oil. In the latter case good separations were observed; this is shown in Table II.

These observations show that when the asphaltenes are separated from the oil, there are hardly any colloids left behind. However, in view of the small density differentials

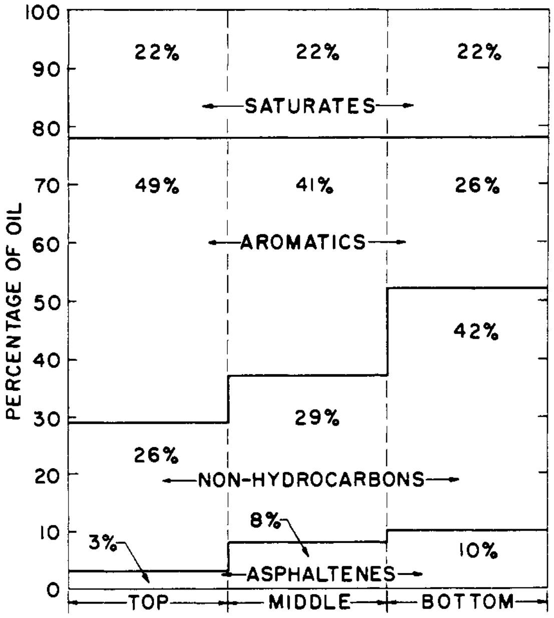

Figure 1. Ultracentrifugation concentrates asphaltenes and nonhydrocarbons from Bachaquero crude oil

Table I. Metals, Nitrogen, and Asphaltenes Contents are Closely Related to the Colloidal Materials Concentrated by Ultracentrifugation

Fraction	Sp. Gr., 60/60 ° F.	Asphaltenes, Wt. %	Metals V, p.p.m.	Metals Ni, p.p.m.	N_2, Wt. %	Atomic Ratio, N to (Ni + V)
			West Texas			
Feed	0.853	1.0	...	...	...	...
Top	0.845	0.2	4.2	1.7	0.074	470
Mid.	0.853	0.4	7.0	2.7	0.086	340
Bot.	0.866	1.2	21.0	5.5	0.121	170
Sepr. factor, bot./top	1.025	6.0	5.0	3.2	1.6	2.8
			Tia Juana			
Feed	0.893	4.9	187	24	0.210	37
Top	0.884	2.6	90	11	0.177	65
Mid.	0.893	4.7	152	17	0.209	46
Bot.	0.905	8.4	220	30	0.290	43
Sepr. factor, bot./top	1.023	3.2	2.4	2.7	1.6	1.5
			Lagunillas			
Feed	0.944	7.8	290	41	...	...
Top	0.943	8.2	250	38	0.325	42
Mid.	0.945	8.6	250	38	0.349	45
Bot.	0.948	9.4	295	42	0.357	39
Sepr. factor, bot./top	1.004	1.1	1.2	1.1	1.1	1.1
			Kuwait			
Feed	0.880	2.57	27	11	0.13	130
Top 1	0.865	0.98	15	4.6	0.09	172
2	0.877	2.09	25	8.4	0.11	124
3	0.878	2.36	31	9.2	0.11	102
4	0.885	3.00	33	10.0	0.13	113
5	0.890	3.68	38	12.0	0.14	105
Bot. 6	0.900	4.93	44	13.0	0.16	105
Sepr. factor, bot./top	1.038	5.1	2.9	2.8	1.8	1.64

between colloidal materials and the medium, the existence of additional colloidal species cannot be excluded on the basis of nonsedimentation.

An additional indication of the colloidal nature of asphaltic materials and its direct realtionship to metals content is shown from carbon residue measurements. This can be shown by plotting the vanadium, nickel, and nitrogen contents of ultracentrifugation fractions from Tatums crude oil against the carbon residues of these fractions. While the exact nature of materials in crude oil which contribute to carbon residues are unknown, the correlation of carbon residue with asphaltenes content has been well established (*6*).

The correlation of nitrogen with asphaltenes supports findings by Ball (*1*), who showed a linear relation between nitrogen and carbon residue. As already mentioned, the latter is related to asphaltenes content.

Although the results are similar, the difference between precipitation of asphaltenes by solvents and their concentration by ultracentrifugation must be emphasized. In a precipitation process, as for example by propane, the polar materials are precipitated. Therefore, metallic constituents, polar hydrocarbons, salts, water, and many other materials, even dissolved ones, are precipitated and may be correlated with each other. This does not prove a physical association of such materials, only a physical similarity. Conversely, by ultracentrifugation, only colloidal materials are concentrated toward the bottom of the tube. Thus, the correlations above actually show a physical association of at least part of the nitrogen, the metals, and asphaltenes.

Ultracentrifugation May Give Clue to Nature of Metals in Oil. Extensive work has been done in the last few years to determine the chemical nature of metals in oil (*4*, *9*). Depending on the source of the crude oil, 10 to 50% of the metals in petroleum exist as porphyrin complexes; the balance is still unidentified. Since the ultracentrifugation data presented here show a relationship between the metals and nitrogen, it was hoped that these data could give a clue about the nature of metals.

If each metal atom was complexed in the oil with a porphyrin molecule, there should be at least four times as much nitrogen in the oil as metals. Actually, there are many times more nitrogen than could be accounted for (Table I). This can only mean that it is possible for all the metals in ratio decreased with increasing asphaltenes and metals, apparently, a major part of the nitrogen is soluble in oil and is not associated with the metals.

If all the metals in the oil can be concentrated by ultracentrifugation in one fraction and the nitrogen content determined, one might be able to assess the portion of the metals existing as porphyrin complexes.

Sulfur Correlates with Apshaltenes; Metals Correlate Better. The West Texas crude oil was centrifugated as previously described, but six samples instead of three were separated from each tube to obtain a wider spread in properties. This study is illustrated in Figure 2, and summarized in Table III with data on Kuwait Oil (specific gravity at

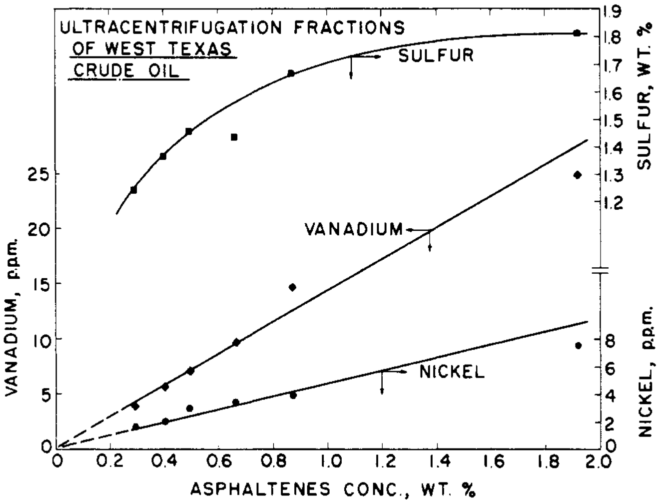

Figure 2. When asphaltenes content approaches zero, sulfur in the oil is still high while the metals are decreased considerably

Table II. Asphaltenes and Vanadium Content after Ultracentrifugation of Tatums Crude and Its Deasphalted Fraction

	Tatums Crude					Deasphalted Tatuams Crude		
Fraction	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.	N_2, wt. %	C Res., wt. %	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.
Feed	4.5	120	58	...	5.8	0.26	14	10.5
Top	3.1	85	43	0.350	4.6	0.22	14	9.8
Middle	4.5	120	56	0.376	5.6	0.21	13	11.3
Bottom	5.7	153	70	0.426	6.8	0.23	13	11.0
Sepr. factor, bot./top	1.8	1.8	1.6	1.2	1.5	1	1	1.1

Table III. Sulfur Distribution in the Different Fractions from Ultracentrifugation

	West Texas Crude				Kuwait Crude			
Fraction	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.	S, wt. %	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.	S, wt. %
Feed	1.0	...	...	1.37	2.57	27	11	2.34
(Top) 1	0.29	4.2	1.6	1.24	0.98	15	4.6	2.22
2	0.40	5.8	2.0	1.36	2.09	25	8.4	2.40
3	0.49	7.2	2.9	1.45	2.36	31	9.2	2.50
4	0.66	9.9	3.5	1.43	3.00	33	10.0	2.56
5	0.87	14.8	3.9	1.67	3.68	38	12.0	2.80
(Bot.) 6	1.92	25.0	7.5	1.81	4.93	44	13.0	2.88
Sepr. factor, bot./top	6.6	6.0	4.7	1.5	5.1	2.9	1.8	1.29

60°/60°, 0.8796). Table III shows that sulfur concentrates in the fractions rich in asphaltenes and metals, but not in the same order of magnitude, the separation factor for the sulfur being much smaller than that for the metals. Extrapolation of the asphaltenes-nonhydrocarbons data shows that at zero asphaltenes concentration, the metals content approaches zero while the sulfur is only partially reduced.

This finding is not unreasonable since one would expect parts of the sulfur compounds to be perfectly soluble in the oil, and others to be associated with the asphaltenes. Only the latter type can move down with the colloids. On the other hand, the metals exist mainly in the asphaltenes and, therefore, follow more closely their concentration pattern.

Extrapolation of the metals curves to zero asphaltenes content for the West Texas oil indicates that this oil, if freed entirely of asphaltenes content, would contain less than 2 p.p.m. of vanadium or nickel. This indicates the likelihood of the presence of small amounts of metals in true solution in the crude oil. This oil contains 12 p.p.m. of porphyrins, as determined by the Groennings method (*5*). Previous work (*3*) has shown that these are present as vanadium and/or nickel complexes in many oils. At least a part of these metal-porphyrin complexes are oil soluble (*4*) and, hence, should not be concentrated by ultracentrifugation. Since 12 p.p.m. of porphyrins could complex about 1 p.p.m. of nickel and vanadium together, the extrapolation appears valid. Similar analysis could not be done on the Kuwait oil because porphyrin data were not available.

As mentioned before, it is important to concentrate metals in a small fraction of the oil in order to associate them with nitrogen and possibly arrive at some way of establishing their nature—e.g., porphyrin complexes or otherwise. This is rather difficult because most of the oils rich in metals and asphaltenes are very viscous. Consequently, sedimentation of colloids is slow and time-consuming. To speed this process, thinners (diluents) or techniques which take advantage of fractionation principles can be employed.

Solvents Speed Separation of Colloids. Previous work (*2*) indicated that Decalin could be used as a diluent for crude oils with a minimum effect on the colloidal system. As shown in Table I, Lagunillas crude oil was so viscous that very little separation was accomplished after a 200-hour period of ultracentrifugation. Accordingly, this oil was diluted to form a 61.6 weight % solution in Decalin, this solution had a viscosity of 18.6 centistokes at 100° F., and a specific gravity of 0.924 at 60°/60° F. The solution then was centrifuged for 100 hours at an average of 80,000 times gravity. After centrifugation, the Decalin was evaporated from the crude and measurements were made. The results of centifugation of Lagunillas crude with and without a solvent are compared in Table IV.

Table IV. Separation of Metals and Colloids Enhanced by Dilution of Lagunillas Crude Oil with Decalin

	Undiluted Lagunillas Crude			Diluted Lagunillas Crude After Solvent Evaporation-		
Fraction	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.	Asphaltenes, Wt. %	V, p.p.m.	Ni, p.p.m.
Feed	7.8[a]	290	41	7.2[a]	213	30
Top	8.2	250	38	5.1	176	26
Middle	8.6	250	38	8.0	...	...
Bottom	9.4	295	42	10.6	280	39
Sepr. factor, bot./top	1.1	1.2	1.1	2.1	1.6	1.5

[a] Slight difference between the properties of the crude oils is mainly due to incomplete evaporation of the Decalin.

In the presence of the solvent, the separation of asphaltenes and metals was almost doubled. The successful use of a suitable solvent shows that it is possible to study the colloidal nature of very viscous oils by the ultracentrifuge.

Asphaltenes May Vary in Vanadium Content. A fractional ultracentrifugation method, involving repeated centrifugation, separation, and recombination, could result in fractions of somewhat different viscosity properties than those separated after a differential (regular) centrifugation (*2*).

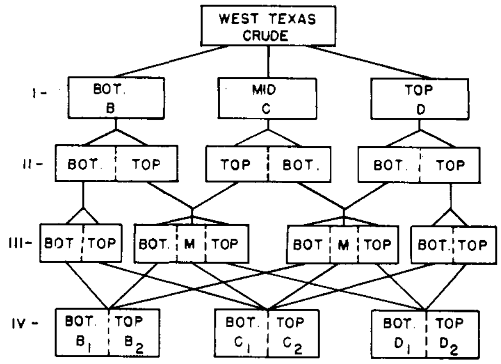

Figure 3. Schematic diagram of fractional ultracentrifugation

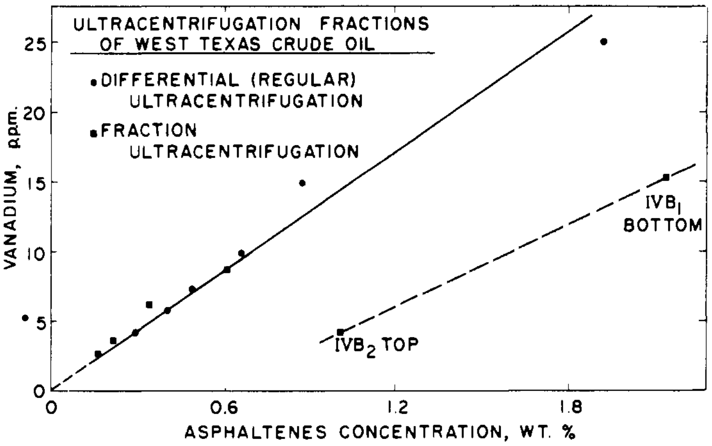

Figure 4. Fractional vs. differential (regular) ultracentrifugation results

Table V. Fractional Ultracentrifugation Method May Permit Separation of Asphaltenes of Varying Vanadium Content

			Metals				
Fraction	Sp. Gr. 60/60 ° F.	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.	N_2, wt. %	Sulfur, wt. %	C. Res., wt. %
Feed	0.853						
IV D Top.	0.840	0.17	2.6	1.0	0.073	1.03	0.7
IV D Bot.	0.851	0.22	3.6	2.2	0.092	1.19	0.9
IV C Top.	0.852	0.34	6.2	2.2	0.114	1.22	1.2
IV C Bot.	1.863	0.61	8.6	3.5	0.134	1.49	1.8
IV B Top	0.866	1.01	4.2	1.7	0.136	1.57	1.4
IV B Bot.	0.878	2.15	15.3	4.8	0.170	1.85	2.6
Sepr. factor, Bot./Top	1.04	12.5	5.9	4.8	2.3	1.8	3.7

A fractional ultracentrifugation of West Texas crude oil (Figure 3) is summarized in Table V. Here, when data from both techniques were plotted on a common basis in Figure 4, the vanadium to asphaltenes ratio was the same in most cases. Only the heaviest portions (IV B) from the fractional technique had a metals content considerably lower than expected. This deviation could be explained either by some analytical or experimental error or by the fact that asphaltenes vary in vanadium content. If this were true, the fractional technique, in addition to speeding separations (compare data in Table I with data in Table V), could probably be used to fractionate asphaltenes.

The carbon residue of the lower centrifuge fractions are higher than those of the top layers and correlate well with asphaltenes and metals content. This is an additional indication that the colloidal particles of petroleum are of an asphaltic nature.

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Metal Content of Twenty-Four Petroleums

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VARIED INFORMATION has been published concerning the metal content of petroleums (*4, 6, 14, 17*), but the data are limited for crude oils from definitely known geographic and geologic sources. The samples analyzed in many instances have been mixtures or have been only partially identified. For this investigation 24 petroleums were collected by the Geological Survey and analyzed semiquantitatively for 27 elements and quantitatvely for vanadium, nickel, copper, and uranium. In addition, they were analyzed by the routine Bureau of Mines crude oil analysis method (*18*). These petroleums can be associated geographically with the oil field and geologically with the producing formation.

For many years the Bureau of Mines at its Laramie, Wyo., and Bartlesville, Okla., Petroleum Research Centers has been studying the properties of crude petroleums from the standpoint of utilization. The Geological Survey has studied the occurrence of petroleum from the standpoint of geochemistry and has been particulary interested in the relationships between chemical characteristics of oils and their geological assocition. The crude oil analyses discussed in this report were made by the Bureau of Mines; trace metal analyses were made by the Geological Survey.

The analytical data were examined for relationships between the four metals. Ash contents of the oils, roughly proportional to the total metal contents, were correlated with carbon residue, nitrogen, and sulfur contents. The effects of the geographical distribution and the geological age of the reservoir rocks were also considered. Although the data are too few to establish definite relationships, apparently the oils from older formations are more uniform in their proportions of contained metals.

A crude oil from Wilmington, Calif., which has been under study by Americal Petroleum Institute Research Project 52 at the Bureau of Mines Laramie Petroleum Research Center, was separated into fractions using solvent precipitation, and adsorption (*10*), and the fractions were analyzed for metals. In this way some information was