Capacity of Petroleum Asphaltenes to Complex Heavy Metals

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In four asphaltic crude oils, the concentrations of nonporphyrin vanadium were found to range from nearly 0 to 784 p.p.m. Most of this metal appeared to be associated with the nonhydrocarbon asphaltic fraction and indicated either variation in the abundance of coordinating sites or different degrees of saturation in respect to the metals. Using an acetylacetonato vanadyl complex as a metal donor, it was found that the asphaltene fractions of the four crude oils would take up amounts of the metal ion ranging up to 2300 p.p.m. and that the amount taken up did not bear any significant relation to the amount of the metal originally present. Uptake or retention of nickel (II) under similar conditions apparently was slight and of copper (II), negligible.

THE FORMS in which vanadium and nickel might occur in crude oils have been discussed almost since the date of the discovery of their occurrence. In 1924 Nellenstyn (*11*) proposed that a part of the metals might be present as inorganic crystals forming the nucleus of colloidal particles. The possibility of organometallo complexes was proposed by Shirey (*16*) in 1931 and confirmed in part by the identification of porphyrin metallo complexes by Treibs.

Until recently, little attention has been paid to the chemical state in which metals not bound to porphyrin might exist. Wolsky and Chapman (*22*) in 1960 revived the inorganic concept, at least for hydrocracked refinery fractions, by stating that the vanadium appeared to be present in the form of oxides, sulfides, and water-soluble compounds. In the same year, Dunning and coworkers (*3*), on the basis of electron spin resonance data, divided the vanadium in crude oils into four categories; volatile and vanadyl—*i.e.*, prophyrin complexes; volatile and nonvanadyl; nonvolatile and vanadyl; and nonvolatile and nonvanadyl. In the following year, on the basis of further ESR studies, Saraceno and coworkers (*15*) and Roberts and coworkers (*14*) presented data indicating that virtually all the vanadium in crude oils exists as vanadyl complexes with an environment similar to that in the etioporphyrin I complex. Extraction studies by Howe and Williams (*10*) in 1960, have indicated that a large part of the nonporphyrin vanadium remains in crude oils after a Treibs-Groennings (*7, 19*) HBr-acetic acid treatment which cleaves the porphyrin complex. Finally in 1962, Yen and coworkers (*23*) proposed that the nonporphyrin metals are chemically associated with the nonhydrocarbon asphaltic fraction, the sites being "holes" in the aromatic clusters; where the "holes" are edged with heteroatoms such as nitrogen, oxygen, or sulfur.

In recent years, attempts have been made to correlate the occurrence of the metals with the history of the crude oils and to explain how and at what period they entered the crude. The findings are contradictory and the conclusions, confusing. Gulyeva (*8*) in 1952 reported that for Russian crude oils from the Carboniferous and Devonian, the V/Ni ratio increased with age. Hodgson (*9*) in 1954, however, reported that for Canadian crudes from the Cretaceous to Devonian, the ratio decreased with age. Witherspoon and Nagashima (*21*) in 1957 reported a nearly constant ratio for Illinois crudes of Pennsylvania, Mississippian, and Devonian age and finally, Demenkova and coworkers (*2*) in 1958 concluded that there was no correlation with age. In respect to origin of the porphyrin metallo complexes, at least, Treibs (*19*) and later Corwin (*1*) believed that the metals entered the porphyrin ring after deposition and burial of the organic detritus. Vinogradov (*20*), however, representing the Russian school, believed that the metal complexes were originally present in the blood and tissues of ancient living organisms.

In the many studies of the occurrence of vanadium and nickel in crude oils, it apparently has been assumed that crude oils are saturated in respect to these metals. Further, very little consideration has been given to the possibility that the number of the coordinating sites and the tenacity with which they bind vanadium and nickel might vary in equivalent cuts of crude oils of different geographic and geologic origin. The investigations reported in this paper represent an initial effort toward a better understanding of these factors concerning the composition and origin of crude oils.

EXPERIMENTAL

Preparation of the Asphaltenes. The four asphaltenes were prepared from samples of the crude oils which, with the exception of the Boscan, had been collected for research purposes in vinyl plastic lined drums. The asphaltene fractions were precipitated by the addition of a tenfold volume of *n*-pentane, washed with additional pentane, and then extracted with the same solvent in a Soxhlet apparatus for 24 hours. To prevent alteration by oxidation, the washed samples were stored as pentane slurries in sealed glass containers until shortly before use.

To determine the proportions of resin and oil, the pentane supernatants from the precipitation of the asphaltenes were stripped of solvent at 80° C. and the resin and oil separated by treatment with a tenfold volume of liquid propane at room temperature in a steel pressure vessel.

Bis-Acetylacetonato Metallo Complexes. The complexes of oxovanadium(IV), or vanadyl, and copper(II) were obtained from the Union Carbide Metals Co. The nickel (II) complex was obtained from the MacKenzie Chemical Works, Inc. All three complexes were used without further purification.

Reaction Mixtures. Each reaction mixture for charging to the washing apparatus contained 6.0 grams of the asphaltene and, where used, approximately 30 mg. (588 μmoles) of the metal as the acetylacetonate complex made up to a volume of 300 ml. in freshly boiled reagent grade benzene. When the metal acetylacetonate is to be included, the asphaltene and the metal acetylacetonate are dissolved in approximately 100 and 150 ml. of benzene, respectively. After complete solution is obtained in both cases, the two solutions are combined and made up to volume. In most instances the mixture was immediately introduced into the extraction apparatus. The time interval between mixing and completion of the first extraction cycle was about 0.5 hour. In those instances where the solutions were to be heated for extended periods of time, sealed glass ampoules were used in which the space above the liquid was filled with high purity nitrogen. In one experiment, a solution of Baxterville asphaltene and nickel acetylacetonate was refluxed for 8 hours.

In those runs designed to test the efficiency of the washing procedure, the asphaltene in the solution was replaced by an equal weight of heavy, white mineral oil.

Aqueous Wash Solutions. Wash water with a minimum concentration of heavy metal ions was considered an absolute essential. Accordingly, laboratory distilled water was passed through an Illco-Way Research Model deionizer. Before adjustment of pH, excess benzene was added to saturate the water. To obtain a pH of 6.0, as indicated by a pH meter, it was only necessary to add a little CO_2 from the air. To obtain pH 2.0, HCl was added until the desired reading was obtained. Examination of the resulting solution by emission spectroscopy indicated vanadium and nickel concentrations of less than 0.1 and 0.2 part per billion, respectively. The $1.0N$ solution, which for HCl corresponds to a pH of approximately 0.1 (*17*) was prepared by addition of the concentrated acid. Adjustment of concentration was made on the basis of titration with standard NaOH solution. No buffers were used owing to the danger of forming complexes with the metal ions.

Removal of Excess Metal. An aqueous washing procedure was used to decompose the excess metal acetylacetonate complexes and to remove the metal from the benzene solution of the asphaltene. To achieve thorough washing without emulsification and subsequent losses of the sample, a countercurrent extractor was used. The design of the apparatus is shown in Figure 1. Briefly, the apparatus consists of a countercurrent extraction column shown in the center, a reservoir and pumping system, shown on the left, for cycling the benzene solution; and a feed reservoir and pump, shown on the right, for replacing the aqueous wash liquid after each passage of the benzene solution.

To charge the apparatus, the aqueous phase was pumped into the extraction column until the level stands just above the inlet tube. The benzene solution next was poured into the reservoir on the left and the connecting tube at the top replaced. With the pump for the aqueous phase turned off, the Teflon bellows pump was turned on and the benzene solution pumped into the extraction column through the coarse sintered glass disk set in the lower section of the column. The benzene solution was thereby broken into droplets which slowly rose through the water to the top of the column. To achieve dispersion of the benzene solution, it was essential to have the sintered glass disk wet by water prior to contact with the benzene solution. Finally, the stand tube which controlled the height of the aqueous phase in the extraction column was so adjusted that a layer of benzene remained in the top of the column providing time for water to separate prior to passage of the benzene solution into the reservoir on the left.

In operation, the benzene solution was pumped through the extraction column at the rate of 16 ml. per minute. After the solution had made one passage or cycle through the extraction column, the Teflon bellows pump was turned off. The finger pump then was started, pumping the aqueous solution from the 5-gal. reservoir into the top of the extraction column. The spent liquid escaped through the stand tube. Pumping was maintained at the rate of 17 ml. per minute, the slow rate being necessary to prevent carryover of droplets of the benzene solution which may have been dispersed in the aqueous phase in the column. When a quantity slightly in excess of that contained in the column had been pumped through, the finger pump was turned off and the circulation of the benzene solution begun by means of the Teflon bellows pump. This alternate cycling of the benzene solution and replacement of aqueous phase were accomplished automatically by means of an interval timer.

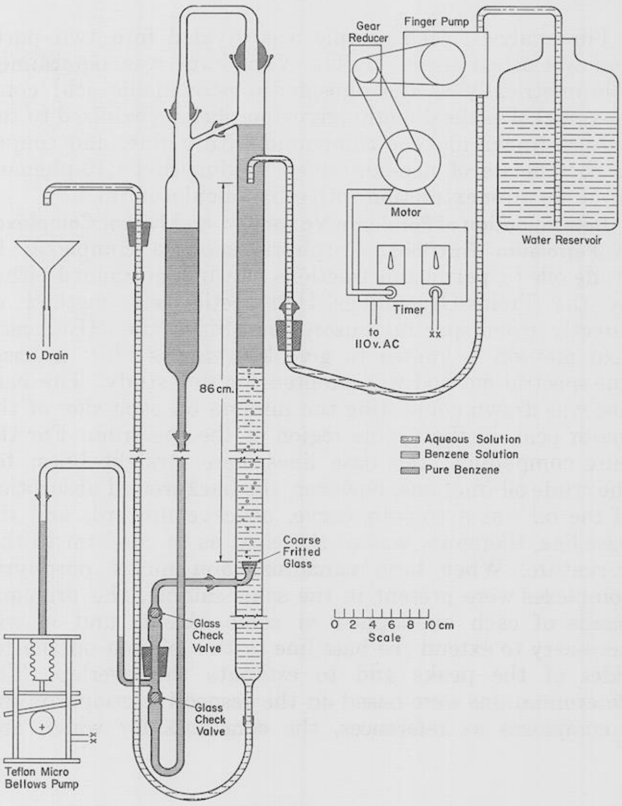

Figure 1. Countercurrent extractor

At the low concentrations of metals under study, consideration had to be given to prevention of accidental contamination. In the extraction, or wash apparatus, the benzene solution came in contact with glass only, and the aqueous solution with only glass and Tygon tubing. The Teflon bellows pump was set up in such a manner that when the bellows was filled with pure benzene, there was an oscillating air gap between it and the check valves, which transmitted the pulse but prevented entrance of the benzene solution into the bellows. After use, the apparatus is cleaned by rinsing with benzene, acetone, benzene, and finally a warm solution of a nonionic detergent to which a few drops of 49% HF had been added. The sintered glass disk withstood about 15 such treatments before replacement became necessary.

Sampling and Analysis for Metals. To remove an aliquot of the benzene solution for analysis, the U tube connecting the top of the column and the reservoir was removed and a 25-ml. sample was withdrawn by means of a pipet. About six samples were taken during an experiment, usually after the first and fourth cycles and then at progressively longer intervals. After about 35 to 40 cycles or about 24 hours of washing, the remainder of the benzene solution was removed, representing the final and larger sample for precise analysis.

The benzene aliquots were centrifuged to remove traces of water, concentrated in a Rinco evaporator, and freeze-dried to a fluffy brown powder.

For analysis, each sample was divided into two parts and wet-ashed using H_2SO_4. Vanadium was determined colorimetrically as the phosphotungstovanadic acid complex; nickel as the dimethylglyoxime chelate, oxidized to the reddish-brown nickelic compound with iodine; and copper as the chelate of neo-cuproine (2,9-dimethyl-1,10-phenanthroline) after extraction with ethanol-chloroform.

Determination of Porphyrin Vanadium and Nickel Complexes in Petroleum Fractions. Porphyrin metallo complexes in crude oils or petroleum fractions can be determined either by the Treibs-Groennings HBr–acetic acid method or directly from spectral absorption. Since the HBr–acetic acid method is known to give low results (*18*), a base-line spectral method was adopted for this study. The base line was drawn connecting the minima on each side of the major peak in the visible region of the spectrum. For the pure compounds, the base lines were straight lines; for the crude oil fractions, however, the background absorption of the oil was a smooth curve, concave upward, and the base line, therefore, was so sketched as to conform to this curvature. When both vanadium and nickel porphyrin complexes were present in the same sample, the principal bands of each overlapped to some extent, and it was necessary to extend the base line to the minima on the far sides of the peaks and to estimate the overlap. The determinations were based on the respective etioporphyrin I complexes as references, the constants for which are:

Solvent	Vanadium λ_{max} 573 mμ $\int a\,d\lambda \times 10^{-5}$	Nickel λ_{max} 555 mμ $\int a\,d\lambda \times 10^{-5}$
n-Hexadecane	3.90	4.19
o-Xylene	3.76	4.08
Methylene chloride	3.65	4.00

Determinations based on the Soret, or Great Peak, at about 400 mμ generally have proved to be less reliable. The apparent advantage in the greater intensity of this peak usually is more than nullified by the much higher absorption of petroleum fractions near the edge of the ultraviolet.

DISCUSSION

Four asphaltic crude oils were studied, the Boscan and La Luna from Venezuela, the Baxterville from Mississippi, and the Belridge from California. These four crude oils were selected as representing a fairly wide variation in both the absolute concentrations of vanadium and nickel and also of the V/Ni ratio.

In Table I are compared the API gravity; Conradson carbon number; proportion of asphaltene, resin, and oil; and the concentrations of vanadium and nickel. Immediately, it can be seen that the concentrations of the two metals correlate with neither the contents of the asphaltic, nonhydrocarbon portions of the crudes—i.e., the asphaltene and resin fractions, nor with gravity or carbon number.

In Table II are listed the concentrations of vanadium present as porphyrin and as nonporphyrin complexes and percentage of the total vanadium in porphyrin combination for the four crude oils and their major fractions. It will be seen that the proportion of the vanadium present as nonporphyrin complexes varies tremendously both for the crude oils and for their respective fractions. In the Baxterville crude oil, virtually all the vanadium is present as porphyrin complexes, while in the Belridge only 53%, and in the Boscan and La Luna only 31% and 27% of the vanadium, respectively, exist in this form. While the highest concentrations of porphyrin vanadium complexes occur in the asphaltene and resin fractions, a much higher proportion of the nonporphyrin vanadium is associated with the asphaltic fractions.

Table I. Vanadium and Nickel Content of Four Asphaltic Crude Oils

Crude Oil	API Gravity[a]	Conradson Carbon, No.	Asphaltene, Wt. %	Resin, Wt. %	Oil, Wt. %	Vanadium, P.P.M.	Nickel, P.P.M.
Boscan	17.2	14.02	18.0	29.4	52.6	1134	108
La Luna	28.4	5.62	4.1	9.1	86.8	208	17.5
Baxterville	16.0	13.75	17.2	8.9	73.9	46.7	19.0
Belridge	13.8	7.03	5.1	18.0	76.9	32.0	120.0

[a] API Gravity = 141.5/(sp. gr. 60°/60° F.) – 131.5.

Table II. Concentrations of Vanadium Complexes, Porphyrin and Nonporphyrin, in Fractions of Four Crude Oils

		Vanadium Concentration, P.P.M.			
	Fraction	Boscan	La Luna	Baxterville	Belridge
Present as porphyrin complexes	Crude oil	350	56	46.7	17
	Asphaltene	868	200	230	180
	Resin	622	460	73	31
	Oil	21.6	9.05	0.56	2.7
Present as nonporphyrin complexes	Crude oil	784	152	~0	15
	Asphaltene	3612	2740	~0	95
	Resin	439	370	~0	58.7
	Oil	9.8	3.3	(0.2)[a]	~0
		Total Vanadium Present as Nonporphyrin Complexes, %			
	Crude oil	69	73	~0	47
	Asphaltene	81	93	~0	35
	Resin		45	~0	65
	Oil		27	+	~0

[a] Limit of detection.

To determine whether and, if so, to what extent petroleum asphaltenes are saturated in respect to heavy metals, it was necessary to devise a method whereby such metals could be introduced into any unoccupied coordinating sites. Several requisites were placed upon the method. Since it is not unlikely that the vanadium and nickel entered both porphyrin and asphalt under similar conditions during genesis of the oil, experimental conditions should be effective for porphyrin metalization, but should at the same time, allow for intimate contact of the vanadium compound with asphaltenes. Further, it must be possible to remove excess of the reagent after reaction without chemical alteration of the asphaltene. This condition precluded the use of high temperatures, strong acids, or halogenated solvents.

The usual method for introducing nickel, vanadium, or other metals into the porphyrin ring consists of bringing together the porphyrin and a soluble inorganic salt of the metal of proper oxidation state in a glacial acetic acid solution. Sodium acetate or pyridine is used as a buffer, the temperature usually being that of boiling acetic acid. However, petroleum asphaltenes and even the resins, are but sparingly soluble in acetic acid. As was shown by Erdman and coworkers (*4*), too much pyridine inhibits complex formation, at least in the case of vanadium. addition of enough benzene to increase sufficiently the solubility of the asphaltene or resin also inhibited the reaction. Metal transfer proved to be a suitable method, using the acetylacetonates as the donor complexes. These complexes of vanadium, nickel, and copper are easily soluble in anhydrous benzene and were demonstrated to be capable of yielding their metal to pure synthetic etioporphyrin I. The use of these and other metal acetylacetonates for the synthesis of porphyrin metallo complexes is the subject of another study. Further, the metal acetylacetonates are are rapidly and completely decomposed by contact with water in the case of the vanadyl complex, or dilute acid in the case of the nickel and copper complexes; the excess metals are then readily extracted.

Aqueous extraction of benzene solutions of petroleum asphaltenes is difficult owing to ready formation of emulsions. To speed the operation and to minimize handling losses, a countercurrent extractor described in the experimental section was devised.

To test the efficiency of the extraction procedure, quantities of white mineral oil equivalent to the quantity of petroleum asphaltene to be used were made up in benzene, contacted in each case with a solution of the particular metal acetylacetonate, and charged to the washing apparatus. At intervals, aliquots of the benzene solutions were removed, the benzene was evaporated off, and the oil residues were analyzed for the metal. In all cases, it was found that washing removed the metals from the mineral oil rapidly and completely.

Two further considerations entered into the plans for experiments involving the asphaltenes. First, porphyrins naturally present in crude oils have always been saturated in respect to vanadium and nickel. If the asphaltenes were not saturated, it would follow that any additional complexes formed with added metal may be less stable than the porphyrin complex. Second, petroleum asphaltenes are believed to be of quite high molecular weight and to be strongly associated in solution (*13*). Consequently, uptake of metal might represent a rather slow process. To explore these eventualities, the conditions of the experiments were varied in certain instances. One variable was the temperature and the time of contact between asphaltene and metal acetylacetonate, it being reasoned that the reaction would be more complete the longer the time and the higher the temperature. The other variable was the pH of the wash water, it being assumed that the weaker complexes would be decomposed by acid.

For the first series of experiments, the Baxterville asphaltene was selected. As shown in Table II, this asphaltene contains little or no nonporpnyrin vanadium in its natural state. Contact times were either short—i.e., approximately 0.5 hour at room temperature, or in one instance a week at 119° C. in a sealed, nitrogen-filled ampoule; or in another, two weeks at 119° C. Washing was carried out at either pH 6, 2, or 0—i.e., a range of 10^6 in the concentration of acid. Attempts to use stronger acid apparently resulted in chemical alteration of the asphaltic substrate since the asphaltene precipitated and could not be re-dissolved in benzene. To determine whether the concentration of the vanadium naturally present in the asphaltene, in this case as nonporphyrin complexes, would be affected by the washing procedure, solutions of the asphaltene in benzene were put through the extraction or washing apparatus.

The results of these first experiments using Baxterville asphaltene and vanadyl acetylacetonate are shown in Figure 2, where the total concentration of vanadium is plotted against the number of washing cycles. The solid horizontal line represents the benzene solution of the untreated asphaltene, and it is evident that washing does not affect the concentration of the vanadium naturally present. The dotted curves which fall rapidly to the base line represent mixtures of white mineral oil and vanadyl acetylacetonate in benzene. The dashed and dot-dashed curves represent mixtures of the asphaltene and vanadyl acetylacetonate. It can be seen that appreciable uptake and retention of vanadium had occurred. The dashed curves represent short, initial contact with washing at pH's of 6, 2, and 0. As anticipated, the retention of the metal decreases with pH. The dot-dashed curves represent long contact at 119° C. Comparison with the short contact curves, washed at equivalent pH's indicate there was no appreciable or consistent time-temperature effect.

Similar experiments were carried out using the Belridge, La Luna, and Boscan asphaltenes. In these asphaltenes

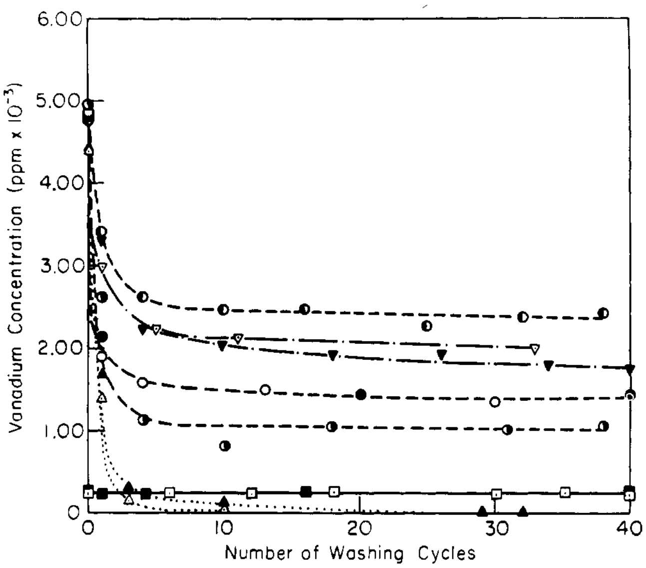

Figure 2. Retention of vanadium by Baxterville asphaltene in benzene solution after washing with aqueous HCl solution

——No vanadium added
Washing at pH 6,■ pH 2,⊡
----After contact with VO(acac)₂, 0.5 hr., room temp.
Washing at pH 6,◐, pH 2,⊙ and ●, pH 0,◑
—·—After contact with VO(acac)₂ 1 to 2 weeks at 119° C.
Washing at pH 6,▽; pH 2,▼
. . . . .Heavy mineral oil substituted for asphaltene
Washing at pH 6,▲; pH 2,△

nonporphyrin as well as porphyrin vanadium complexes are present and the absolute amounts of both total and nonporphyrin vanadium vary tremendously. In fact, the concentrations of naturally occurring nonporphyrin vanadium in the La Luna and Boscan asphaltenes exceeds the total concentration of vanadium in the Baxterville after artificial saturation even at pH 6.

The curves for the experiments using Belridge, La Luna, and Boscan asphaltenes and vanadyl acetylacetonate are shown in Figures 3 and 4. The horizontal lines show that none of the natural vanadium is removed by the washing procedure at a pH as low as 2, despite the fact that considerable amounts of the vanadium present is of nonporphyrin type. The remaining curves in each figure reveal that large additional uptakes of metal had occurred—i.e., that these asphaltenes also are not saturated in respect to vandium.

In Table III the data for the experiments involving the four asphaltenes and vanadyl acetylacetonate are summarized. The total concentrations of vanadium after saturation under a given set of conditions differ greatly, suggesting that the total number of coordinating sites also differ from asphaltene to asphaltene depending upon its source. On the other hand, there appears to be a certain degree of constancy in respect to the amount of additional vanadium taken up. Whether this situation is generally true for petroleum asphaltenes remains to be seen. The results of these experiments, however, suggest the interesting geochemical hypothesis that coordinating sites are formed slowly during the genesis of the asphaltene perhaps through dehydrogenation of condensed naphthenic structures containing heteroatoms such as nitrogen. While the crude oil is dispersed in the source rock and in intimate contact with ground waters, newly formed coordinating sites would be rapidly filled with metal. After accumulation in the reservoir as a discrete oil phase, uptake of metal necessarily would be slower, and the asphaltene fraction of the crude would become progressively less saturated in respect to metals. The degrees of undersaturation of the four crudes, therefore, might be interpreted as indicating that conditions in the respective reservoirs were quite similar insofar as chemical alteration of the asphaltic fraction of the crude was concerned.

A condition imposed by the above hypothesis is that asphaltenes in hydrocarbons solution must be capable of absorbing vanadium from aqueous solutions. Observations by Goldschmidt (*6*) and Pommer (*12*) indicate that in the earth, inorganic vanadium in intimate contact with organic matter exists in the 4+ or vanadyl state of oxidation.

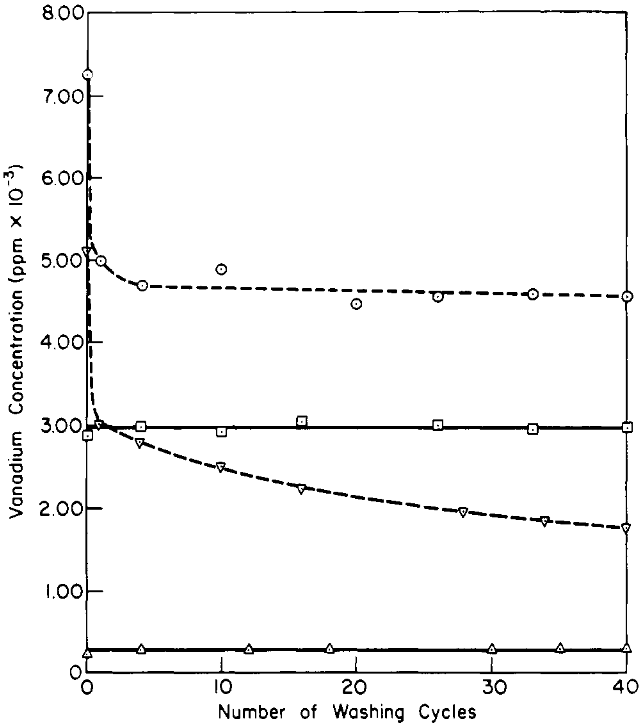

Figure 3. Retention of vanadium by Belridge and La Luna asphaltenes in benzene solution after washing and aqueous HCl of pH 2.0

——No vanadium added
Belridge asphaltene, △
La Luna asphaltene ⊡
----After contact with VO(acac)$_2$, 0.5 hr., room temp.
Belridge asphaltene, ▽
La Luna asphaltene, ⊙

Preliminary experiments performed in this laboratory have shown that asphaltenes in benzene solution, when dispersed in dilute solutions of inorganic vanadyl salts, do indeed take up vanadium slowly.

In respect to the synthesis of porphyrin metallo complexes, Erdman and coworkers (*5*) have shown that the vanadium complex, despite its stability, forms rather slowly compared to, say, nickel. This difference in rate has been attributed to the fact that the vanadyl ion, being unsymmetrical, must approach the coordination site in the porphyrin ring with a particular orientation. The same

Table III. Natural Vanadium Content of Several Asphaltenes and Their Degree of Undersaturation in Respect to the Metal

	Concentration of Vanadium, P.P.M.							
			After Washing at					
	Natural		pH 6		pH 2		pH 0	
Sample	Total	Nonporphyrin	Added	Total	Added	Total	Added	Total
Baxterville	230	0						
0.5 Hr. at room temp.			2150	2380	1170	1400	810	1040
1-2 Wks. at 119° C.			1730	1960	1530	1760		
Boscan	4480	3612						
0.5 Hr. at room temp.					1600	6080	980	5460
1-2 Wks. at 119° C.					920	5400		
La Luna	2940	2740						
0.5 Hr. at room temp.					1580	4520		
Belridge	275	95						
0.5 Hr. at room temp.					1495	1770		

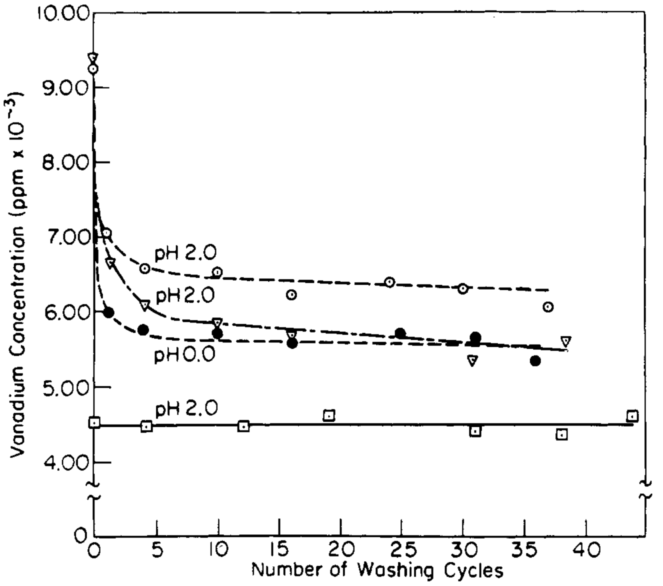

Figure 4. Retention of vanadium by Boscan asphaltene in benzene solution after washing with aqueous HCl solution

——No vanadium added

----After contact with VO(acac)$_2$, 0.5 hr., room temp.

—•—After contact with VO(acac)$_2$, 2 weeks at 119° C.

reasoning applies to the addition of these metals to asphaltenes; hence, it seemed reasonable to expect that nickel and copper should be taken up rather more rapidly. As shown in Figures 5 and 6 and by the numerical data in Table IV, if any of these metals were taken up, they were to a very large extent rapidly lost upon washing. While not inconsistent with the generally low concentration levels for these metals in crude oils, the factors controlling uptake or stability merit further study.

Thus far, no chemical distinction has been implied between the nonporphyrin vanadium complexes already present in the asphaltenes and those formed through saturation by vanadyl acetylacetonate. As pointed out, two groups of workers had found that all the vanadium in crude oils gave an ESR signal similar in shape and intensity to that of synthetic etioporphyrin. ESR examination of freshly prepared Boscan and Baxterville asphaltenes showed vanadyl absorptions in accord with this concept. After saturation with vanadium by contact with vanadyl acetylacetonate and removal of the excess acetylacetonate by washing, it was discovered that the ESR signal had not increased in intensity in proportion to the increase in the total amount of vanadium as indicated by chemical analysis. Whether the apparent disappearance of the ESR signal for the added vanadium is to be attributed to a change in oxidation state of the metal, symmetry factors, or other effects remains to be determined. Work on this problem now is underway.

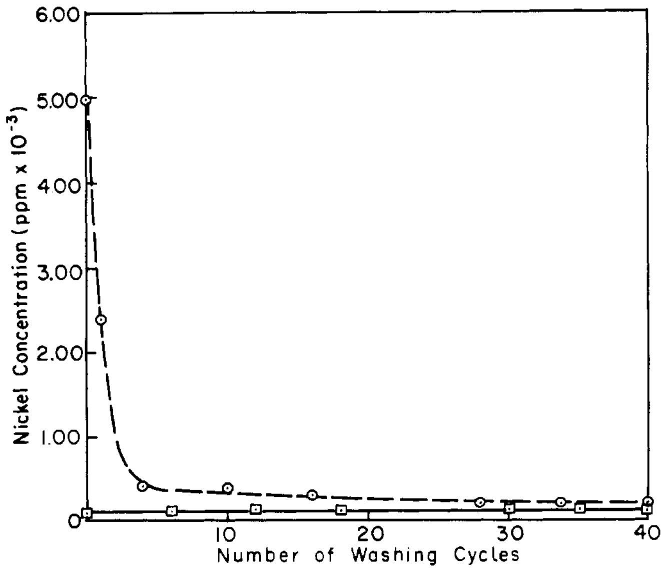

Figure 5. Retention of nickel by Baxterville asphaltene in benzene solution after washing with aqueous HCl of pH 2

——No nickel added

– –After refluxing with Ni(acac)$_2$, 8 hr. at 80° C.

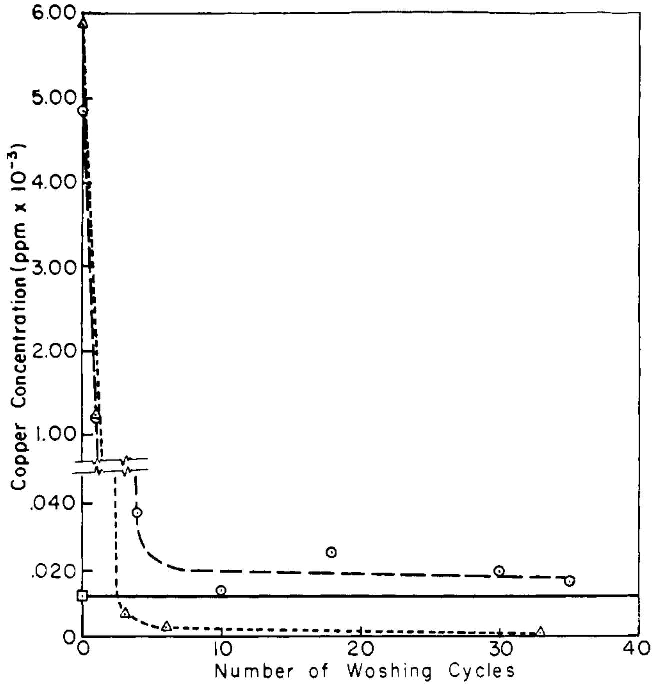

Figure 6. Retention of copper by Baxterville asphaltene in benzene solution after washing with aqueous HCl of pH 2

——Natural copper content

– –After contact with Cu(acac)$_2$, ½ hr. at room temp.

----Heavy mineral oil substituted for asphaltene

Table IV. Natural Nickel and Copper Content of Baxterville Asphaltene and Its Degree of Undersaturation in Respect to the Metal

		Concentration of the Metal, P.P.M.		
			After Washing at pH 2,	
Contact Conditions	Metal	Natural	Added	Total
8 Hr. at 80° C.	Ni	120	70	190
0.5 Hr. at room temp.	Cu	12	5	17

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Pyrolysis of *n*-Butane in a Differential Flow Reactor

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The thermal decomposition of *n*-butane has been studied in the very low conversion region, 0.05 to 5%, in an isothermal flow reactor. The analytical problem was solved by the very successful application of a gas liquid chromatographic technique. An inherent weakness in the usual procedure of extrapolating relatively high conversion data to estimate incipient conversion mechanisms is demonstrated by the results. On the basis of the measured product distributions at these low conversions, it is possible to confirm earlier suggestions concerning the reaction mechanism and kinetics.

THERMAL decomposition of light hydrocarbons has been studied extensively from the theoretical as well as the industrial point of view. Considerable work has been done on the pyrolysis of *n*-butane because of the intermediate complexity of the product mixtures obtained. Moreover, the conversion to useful chemical intermediates of the excess quantities of this material produced during certain seasons has been a spur to research in this area.

Most of the early work was carried out in the low temperature region between 450° and 650° C. and has been carefully reviewed by Steacie (*10*). In the investigations involving determinations of the initial products of decomposition, conflicting results were recorded because of the necessity for extrapolating relatively high conversion data to obtain a measure of the product distributions in the incipient conversion region. The few low conversion data reported by Crawford and Steacie (*3*), suffer from incomplete analyses.

The present work demonstrates an approach which may be used to overcome these difficulties and to obtain a better estimate of the reaction mechanism and kinetics.

EXPERIMENTAL

The reactor used in this study was a 1.3-cm. I.D. Vycor tube, 96% silica, with an effective volume of 17.15 cc., mounted coaxially in the central zone of a 16-inch furnace. Integral parts of the reactor assembly were inlet and outlet quartz capillary tubes which functioned, respectively, for

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