Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.14; H, 5.94; N, 9.22.

3-Ethyl-3, 7-diphenyl-1, 2, 3, 4-tetrahydro-1, 4-diazepin-5-one (VIII). A solution of 3 grams (0.01 mole) of VII in 200 ml. of absolute alcohol was hydrogenated at room temperature and 38.5 pounds pressure using ½ tsp. Raney nickel as the catalyst. The theoretical amount of hydrogen was absorbed within 24 hours. The mixture was filtered, and the filtrate was evaporated to dryness. The solid residue was recrystallized from alcohol, to give 1.1 grams (38%) of a white solid, m.p. 202–204°. The analytical sample melted at 203–205.5°, and showed bands in the infrared ($CHCl_3$) at 6.18 and 6.30 μ (shoulder), and absorbed in the ultraviolet region at $\lambda_{\max}^{MeOH}$ 228 (ϵ17,100) and 304 mμ (ϵ11,900); and $\lambda_{\max}^{MeOH,\,HCl}$ 244 (ϵ13,650) and 314 mμ (ϵ15,300).

Anal. Calcd. for for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58. Found: C, 77.50, 77.76; H, 6.59, 6.97; N, 9.56.

Hydrochloride. The hydrochloride of the above diazepinone was prepared in alcohol and recrystallized from alcohol-ether, m.p. 228–232° (dec.)

Anal. Calcd. for $C_{19}H_{21}N_2OCl$: C, 69.39; H, 6.44, N, 8.25; Cl, 10.78. Found: C, 68.96, 69.20; H, 6.86, 6.79; N, 8.29; Cl, 10.49.

ACKNOWLEDGMENT

We wish to thank L. M. Brancone and associates for the microanalytical data, William Fulmor and associates for the spectral data, and Edward Ruso for the preparation of 2-amino-2-phenylbutyronitrile hydrochloride.

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RECEIVED for review August 12, 1964. Accepted January 27, 1965.

Reductive Desulfuration on Vanadium and Metalloporphyrin Contents of Fractions from Boscan Asphaltenes

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Treatment of fractions derived from Boscan asphaltenes with lithium-ethylenediamine, with Raney nickel, and by electrolysis in lithium chloride–ethylenediamine effected reduction, desulfuration, decrease in vanadium and metalloporphyrin contents, and altered solubilities. Loss in vanadium correlated linearly with loss in metalloporphyrins. Correlation of extent of reduction and loss of vanadium and a similar relationship of extent of desulfuration and loss of vanadium were made. An association of nonporphyrin vanadium compounds with sulfur compounds was suggested.

THE USE of lithium metal in ethylenediamine (EDA) as a reducing agent has been demonstrated (*9*) to be effective in decreasing the sulfur content of coals. This finding suggested the application of this reagent to petroleum fractions to effect the same type of reductive desulfuration, but in addition follow the fate of vanadium metal and metalloporphyrins. Should any relationships emerge, such data could provide clues relating to the forms of occurrence of vanadium in crude oils.

Fractions derived from Boscan (Venezuela) crude oil were used in this investigation since the parent material is rich in vanadium, about 1200 p.p.m.

EXPERIMENTAL METHODS

Pentane asphaltenes, 30 grams, from Boscan crude oil was dispersed in 2625 ml. of pyridine by stirring for 1 hour, and the resulting solution was filtered through cotton to remove extraneous debris. (The rate of filtration through paper or sintered glass was very slow.) While the filtrate was being stirred, 26.5 ml. of water was added, and the resulting mixture was allowed to stand near 0° C. for 1 to 2 days. The suspension was filtered through cotton, and the filtrate was again passed through the same cotton mat. The solid on the cotton was collected and dried to provide about 8 grams of porphyrin-poor (Por-P) asphaltenes. More water, 1286 ml. (combined volume of water is ⅓ of the total volume of water and pyridine introduced), was added to the filtrate, and the resulting suspension was allowed to stand near 0° C. for 1 day. The mixture was again filtered twice through cotton, and the brown solid on the

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Table I. Reductive Desulfuration of Boscan Asphaltene Fractions with Li-EDA

Run No.	Sample	Sample Wt., G.	EDA Vol., Ml.	Li Wt., G.	React. Time, Hrs.	Material Recovery, %		Analysis									
								V, μM/G.		Porphyrin, μM/G.	C, %		H, %		S, %	
						Pyr-S	Pyr-I	Pyr-S	Pyr-I	Pyr-S	Pyr-S	Pyr-I	Pyr-S	Pyr-I	Pyr-S	Pyr-I
1	Por-P asphalt.[a]	6.13	500	6.0	6	12	90	45	63	10.2	69.8	79.0	8.2	8.6	3.3	5.7
2	Pyr-I run 1	4.73	400	6.0	7	8	91	27	51	6.2	78.8	78.8	10.2	8.6	2.4	4.3
3	Pry-I run 2	3.73	320	6.0	7	13	86	27	43	7.1	76.8	79.4	9.8	9.2	2.5	3.4
4	Por-P asphalt.	1.20	150	0.5	2	48	45	60	75	10.2	80.4	79.5	8.8	8.2	6.6	6.8
5	Por-P asphalt.	1.20	150	1.0	2	42	57	50	72	8.8	80.1	78.7	9.2	7.9	5.7	6.7
6	Por-P asphalt.	1.20	150	2.0	2	30	69	47	65	8.5	78.8	79.8	9.1	8.1	5.0	6.5
7	Por-P asphalt.	1.20	150	3.0	2	21	77	45	61	8.1	80.4	77.4	10.1	8.4	3.8	6.2
8	Por-P asphalt.	1.20	150	4.0	2	15	83	44	60	7.9	81.0	72.1	10.8	7.7	2.6	5.4
9	Por-P asphalt.	5.99	600	21.0	4	29	70	28	74	9.9	69.3	...	8.8	...	1.0	...
10	Pyr-S run 9	1.08	170	2.5	3	83	3	22	...	7.8	78.2	...	10.3	...	1.8	...
11	Pyr-S run 10	0.25	50	0.7	2	80	16	21	...	7.4	77.2	...	10.9	...	0.84	...
12	Por-P asphalt.	5.30	500	20.0	6	41	69	40	50	7.5	...	...	...	...	...	...
13	Pyr-S run 12	0.64	100	2.5	3	91	5	24	...	8.7	76.2	...	10.1	...	1.7	...
14	Por-P asphalt.	1.89	150	3.0	2	41	58	38	61	7.3	72.6	74.1	8.9	8.7	2.8	4.5
15	Por-P asphalt.	3.54	270	5.3	3.5	27	75	63	74	9.2	...	...	...	...	...	...
16	Pyr-I run 15	1.34	100	1.7	5.0	39	58	63	40	8.9	...	...	...	...	...	...
17	Pyr-I run 16	0.46	50	18.0	4	16	85	21	40	5.6	...	74.0	...	9.0	...	2.5
18	Pyr-I run 17	0.27	40	1.0	4	20	74	31	24	...	...	74.1	...	9.1	...	2.2
19	Por-R asphalt.[b]	3.12	250	5.0	3	96	3	47	59	33	76.0	...	8.7	...	4.2	...
20	Pyr-S run 19	2.26	280	4.0	4	74	24	28	...	21	76.1	...	8.9	...	3.0	...
21	Pyr-S run 20	0.78	120	3.0	3	84	14	15	...	14	75.5	...	10.0	...	2.6	...
22	Por-R asphalt.	2.72	200	2.5	2	88	10	50	49	35	75.7	...	8.4	...	5.1	...
23	Pyr-S run 22	1.78	200	8.0	5	55	43	11	...	10	80.8	...	10.4	...	2.0	...
24	Por-R asphalt.	1.45	130	4.0	4	61	38	43	48	33	76.2	72.4	9.5	8.5	3.7	5.2

[a] All Por-P asphaltenes (except sample in runs 14 and 15) contained: 80.9% C, 8.06% H, 1.8% N, 6.9% S, 75.8 μM/g. V, 10.4 μM/g. metalloporphyrins, and 1.34% ash. Por-P asphaltenes in runs 14 and 15 contained: 79.6% C, 7.85% H, 2.6% N, 7.2% S, 78.1 μM/g. V, 15.4 μM/g. metalloporphyrins. [b] Por-R asphaltenes contained: 76.5% C, 7.9% H, 6.4% S, 2.8% N, 53 μM/g. V, and 37.6 μM/g. metalloporphyrins.

filter was discarded. To the filtrate, 1312 ml. of carbon tetrachloride was added, and the aqueous phase was separated and discarded. The pyridine–carbon tetrachloride solution was placed in a rotary evaporator to yield about 3 grams of porphyrin-rich (Por-R) asphaltenes.

The Por-P asphaltenes were placed in a Soxhlet extractor and leached with boiling 2-methoxyethanol for 1 day to yield modified Por-P asphaltenes, somewhat lower in metalloporphyrin content, with no observable loss in weight.

Exposure of all petroleum samples to the atmosphere and light was minimized. A given sample was processed with a minimum time interruption. No observable changes were found in solubilities of starting materials over the period of this investigation.

Ethylenediamine was treated with sodium metal and distilled prior to use. Etioporphyrin I was prepared by the two-step synthesis (*4, 5*) from 3-ethyl-2,4-dimethylpyrrole (*6*) and metalated (*13*) with vanadyl sulfate. Raney nickel (*8*) was prepared by the usual method and applied to petroleum materials as previously described (*10*). Metalloporphyrin determination (*12*), vanadium determination (*14*), reduction with lithium-ethylenediamine (*9*), and the electrolytic reduction (*11*) followed methods previously described.

RESULTS AND DISCUSSION

Pentane asphaltenes from Boscan crude were subjected to a pyridine-water partitioning treatment to obtain two fractions. One contained 38μ moles per gram of metalloporphyrins and 53μ moles per gram of vanadium, and the other 11 or 15μ moles per gram of metalloporphyrins and 76 or 78μ moles per gram of vanadium. These fractions are labeled porphyrin-rich (Por-R) and porphyrin-poor (Por-P) asphaltenes, respectively. Enrichment in vanadium is reversed for the two fractions. Accordingly, the non-porphyrin metal compounds are enriched in the Por-P asphaltene fraction.

The reductive desulfuration procedure previously described (*9*) was followed. Processed materials were separated into pyridine-soluble (Pyr-S) and pyridine-insoluble (Pyr-I) fractions. Most of these were analyzed for V, S, C, H, N, and ash. The Pyr-S fraction was also analyzed for metalloporphyrins by the direct integral method (*12*). The insolubility of the Pyr-I fractions precluded this determination by this method. In a few instances the aqueous acid wash, obtained in processing, was analyzed for vanadium content. In general, a satisfactory material balance was found for this element. Total material recovery, the combined weights of the Pyr-S and Pyr-I fractions, in general varied about 5% from the sample weight.

Analytical data obtained are summarized in Table I. Ash and nitrogen content were not included since these figures varied appreciably depending upon the processing conditions applied following the reaction. Ash was found in amounts between 1 to 5%, and nitrogen between 2 to 4%. Ash content tended to be particularly high in the Pyr-I fraction, probably attributable to the difficulty encountered in the complete removal of lithium compounds from this insoluble portion. The complete removal of EDA from coal-like materials is not possible (*9*). Accordingly, all figures for nitrogen content were found to be high. No attempt was made to compensate for these discrepancies in the analytical values for metalloporphyrins, vanadium and sulfur, since any corrections involved would be small.

Among the variables of concern in this reaction is the ratio of sample to Li-EDA. Clearly, larger proportions of lithium metal provided for a higher degree of reductive desulfuration (compare runs 4 to 8, and 1 and 9). Another complication attending this reaction is the competitive formation of *N*-lithioethylenediamine. Following the pro-

Table II. Reductive Desulfuration of Boscan Asphaltene Fractions by Other Methods

Run No.	Sample	Sample Wt., G.	Solvent, Ml.	Reducing Conditions	React. Time, Hrs.	Material Recovery, %		V, μM/G.		Porphyrin, μM/G.	C, %		H, %		S, %	
						Pry-S	Pyr-I	Pyr-S	Pyr-I	Pyr-S	Pyr-S	Pyr-I	Pyr-S	Pyr-I	Pyr-S	Pyr-I
25	Por-P asphalt.	5.21	30 C_6H_6 + 250 EtOH	15 g. Raney nickel	6	82	...	79	...	10.2	...	...	...	...	...	...
27	Por-P asphalt.	2.52	80 C_6H_6 + 160 EtOH	13 g. Raney nickel	6	89	...	69	...	9.8	78.0	...	8.3	...	5.5	...
27	Por-P asphalt.	3.13	140 C_6H_6 + 70 EtOH	13 g. Raney	6	61	...	37	...	7.5	78.0	...	8.3	...	5.6	...
28	Pyr-S run 12 (Table I)	0.71	7 C_6H_6 + 55 EtOH	4 g. Raney nickel	5	30	...	60	...	8.5	74.9	...	8.5	...	3.0	...
29	Pyr-S run 12	0.63	50 EDA	1.5 g. Li	5	72	...	28	...	6.3	75.0	...	9.9	...	2.0	...
30	Por-P asphalt.	1.28	170 EDA	Electroreduction[a]	18	47	45	67	25	10.3	78.5	79.6	8.1	12.5	6.9	1.6
31	Por-R asphalt.	1.15	170 EDA	Electroreduction	5	91	9	69	8	37	78.9	74.1	8.5	15.4	6.7	0.9
32	Por-R asphalt.	1.15	170 EDA	Electroreduction	18	87	13	66	8	29	72.8	69.7	8.5	14.4	6.6	>0.5
33	Pyr-I run 12 (Table I)	1.02	170 EDA	Electroreduction	26.5	1	98	...	55	4.2	...	81.2	...	9.1	...	4.9
34	Pyr-I run 33	0.85	170 EDA	Electroreduction	48	1	102	...	51	...	...	78.2	...	8.9	...	4.8

[a] Conditions used in electroreduction: temperature, 38–40° C.; amount LiCl, 2.4 grams; power supply, 36 volts and 2 amp.; graphite cathode and platinum anode.

cedure described (*9*) for coal, series of runs were made in which a given material was reprocessed (runs 1-3, 9-11, 15-18, 19-21, and 23-24). In general, a reaction period of 2 hours provides much the same degree of reductive desulfuration as longer periods. A series of runs (1 to 3) were carried out at 82° C. instead of at 92° C. as used in all other cases. Data obtained were indistinguishable, although the rate of formation of *N*-lithioethylenediamine is appreciably influenced by the temperature (*1*).

Two other reductive methods were also studied for comparative purposes (Table II). Raney nickel in varying proportions of benzene and ethanol (runs 25 to 28) was applied. No useful information relating to the Pyr-I fractions was obtained because the removal of the catalyst from this insoluble material was not feasible. The efficiency of reductive desulfuration by Raney nickel was distinctly lower than the Li-EDA reagent. (Compare runs 28 and 29, the latter included for this comparative purpose.) The second approach utilized an electrolytic procedure, previously applied to coal (*7*). The method of Sternberg, Markby, and Wender (*11*) was applied to both Por-P and Por-R fractions as well as some Pyr-I portions derived from the former. The extent of reductive desulfuration was distinctly greater than found with Li-EDA in the Pyr-I but not the Pyr-S fractions.

The data given in Tables I and II were analyzed in several ways. Assuming that the pyridine-water partitioning procedure provided a reasonable separation of major types of compounds present in Boscan asphaltenes, data obtained from the Por-P and from the Por-R asphaltenes may be treated in the two categories, as a first approximation. Clearly, Pyr-S and Pyr-I portions obtained from the parents should be different, but variances in properties are likely to be less important. Data obtained from the electrolytic reduction process follow a distinctly different pattern. These will be considered separately and compared with information derived from the other two reduction methods.

A plot of metalloporphyrin and vanadium contents (Figure 1) for both Por-P and Por-R asphaltenes demonstrated an excellent linear correlation. Loss of vanadium in the Pyr-S fractions paralleled loss of metalloporphyrins in these portions. Data for Pyr-S fractions derived from both Pyr-I or Pyr-S portions are included as well as those from Raney nickel reduction in this correlation. Etioporphyrin I and vanadyl etioporphyrin I were treated with Li-EDA and found to undergo changes leading to loss of Soret absorbance. The free porphyrin was destroyed the more readily. Considerable amounts of lithium were required to effect these reactions. Similar observations have been made on vanadyl etioporphyrin I by Eisner (*3*). The ability of Raney nickel to adsorb and probably reduce metal complexes of etioporphyrin I has been reported by Dean and Whitehead (*2*).

A comparison of extent of loss of vanadium with extent of reduction was made. Extent of reduction was calculated following a method (*9*) which assumes no loss of nitrogen in this reductive desulfuration process. Using Por-P asphaltenes, data obtained provided a plot (Figure 2) showing a linear relationship between loss of vanadium and extent of reduction. The Por-R asphaltenes provided different data (Figure 3). This material has approximately 66% of its vanadium in the form of metalloporphyrins, assuming the ratio of vanadium to nickel porphyrins to be 13 (*12*). The Por-P asphaltenes has less than 13% of its vanadium in the form of metalloporphyrins. Release of vanadium from metalloporphyrins might be expected to occur with a given degree of reduction, different from that required for nonporphyrin vanadium compounds.

A comparison of extent of vanadium loss with extent of desulfuration is depicted in Figures 4 and 5. Within runs (4 to 8, Table I) in which the Por-P asphaltenes were processed with different amounts of lithium metal as the only variant, a better correlation was observed. The same applied to comparisons of runs made in series when each group was treated separately. Data obtained were assumed to represent a summation of two different processes. Those reactions leading to the release of vanadium from nonporphyrin metal compounds with concomitant decrease of sulfur were presumed to precede the release of vanadium from vanadyl porphyrins. This assumption was suggested by the observation that destruction of model metalloporphyrins by Li-EDA requires relatively high concentrations of lithium metal.

Changes in extent of pyridine solubility of a given material followed an unusual pattern. Other investigators (*7, 9*) studying coal and its extracts demonstrated that treatment with Li-EDA increased pyridine solubility; electrolysis with lithium chloride in EDA effected a greater change when reduction was carried to about the same extent. Both Por-P and Por-R asphaltenes are totally dispersable in pyridine prior to treatment. Reaction of the Por-P asphaltenes with increasing amounts of lithium increased the percentage of the Pyr-I portion (runs 4 to 8, Table I). However, a given Pyr-I portion when reprocessed gave some Pyr-S material (runs 2, 3, 16 to 18). Similarly, Por-R asphaltenes were reductively desulfurized to yield mainly Pyr-S material but also some Pyr-I (runs 19, 22, 24). The Pyr-S portion so obtained then again provided a Pyr-I fraction (runs 20, 21, 23). Raney nickel treatment gave

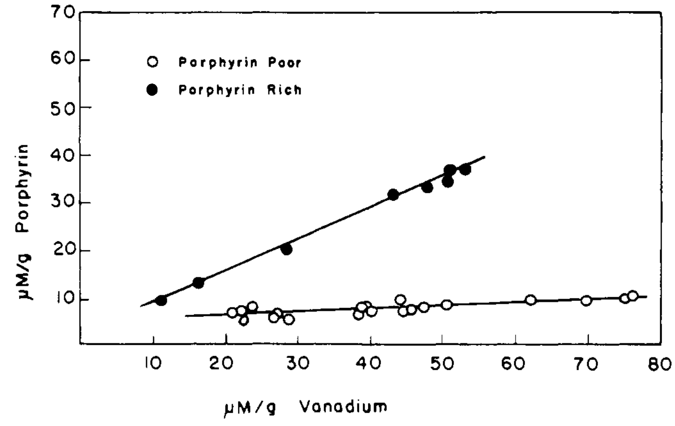

Figure 1. Decreases in metalloporphyrin and vanadium contents following treatment of Por-P and Por-R asphaltenes with Li-EDA and with Raney nickel

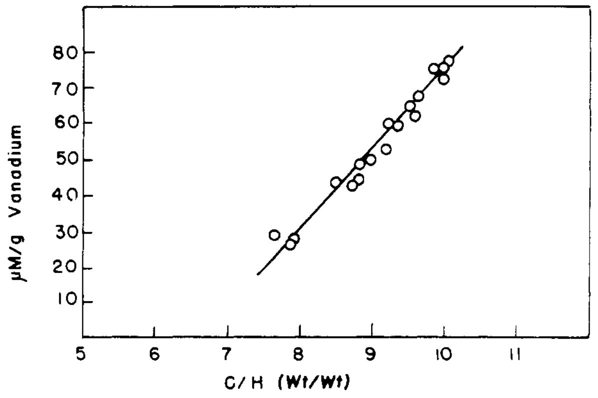

Figure 2. Correlation of loss in vanadium with reduction of Por-P asphaltenes treated with Li-EDA and with Raney nickel

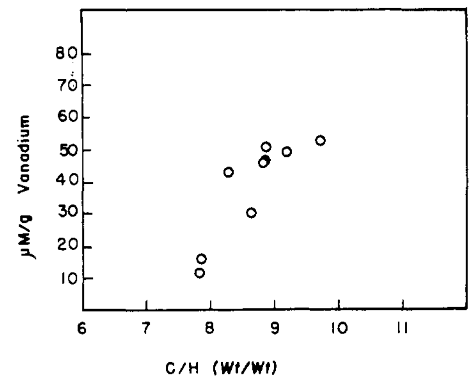

Figure 3. Correlation of loss in vanadium with reduction of Por-R asphaltenes treated with Li-EDA

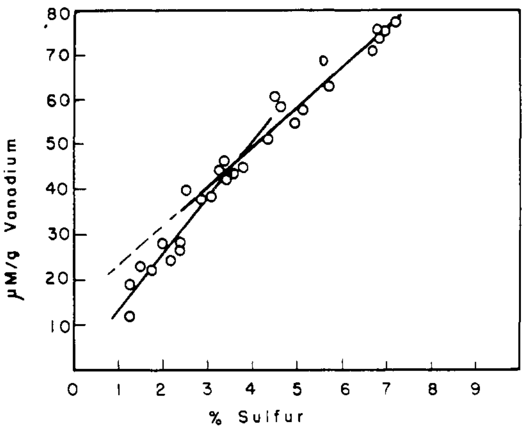

Figure 4. Correlation of loss in vanadium with desulfuration of Por-P asphaltenes treated with Li-EDA and with Raney nickel

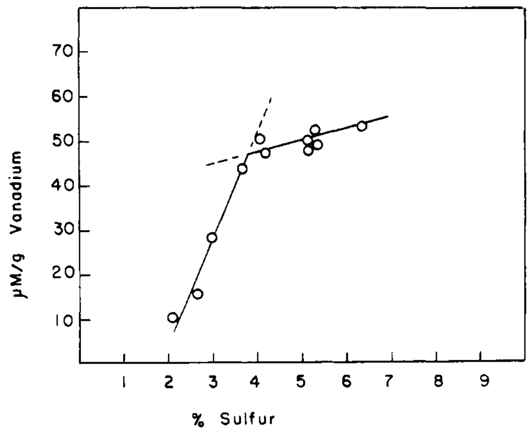

Figure 5. Correlation of loss in vanadium with desulfuration of Por-R asphaltenes treated with Li-EDA and with Raney nickel

incomplete recovery in the Pyr-S fraction, leaving the Pyr-I combined with the spent catalyst.

The solubility changes observed were clearly unexpected. The data suggest a heterogeneous distribution of types of compounds with the more highly condensed and less soluble ones concentrated in varying amounts, intermixed with the dispersing phase to form colloidal particles. The Por-P portion should contain more of the former than the Por-R portion since these materials were separated utilizing solubility differences. The fact that Li-EDA and Raney nickel provided similar results suggests that the course of the reactions is controlled primarily by accessibility, the molecules in the exterior parts of the particles would be desulfurized and lose aromaticity to become less polar and thus poorer dispersing agents. Thus, Pyr-I portions would result from both Por-P and Por-R asphaltenes. Reductive desulfuration of more highly condensed systems can form Pyr-S materials by the buckling of aromatic rings and allowing penetration of solvent molecules (*9*) or by reducing molecular size by desulfuration. There is also the possibility of the presence of areas of dispersed phases in interior portions of the condensed phase. These may become exposed following reaction.

Analytical data describing vanadium and sulfur contents demonstrate that these elements are contained in larger amounts in the Por-P than in the Por-R asphaltenes, and also with just a few exceptions, in each Pyr-I portion than in the corresponding Pyr-S fraction. If the reductive desulfuration process by Li-EDA or Raney nickel is largely controlled by the availability mechanism described, and the natural vanadyl prophyrins require higher concentrations of reducing agent to effect demetalation, then the simultaneous loss of sulfur and vanadium suggests that compounds containing nonporphyrin vanadium must occur throughout the colloidal particles together with sulfur compounds in a manner that the ratio between these two elements is nearly equal. Polar metal compounds may be highly solvated by sulfur compounds.

Electrolytic reduction provided different data. Vanadium and sulfur contents are appreciably smaller and extent of reduction much greater in the PI portions, but changes in the PS portions are relatively minor. However, more highly condensed material as represented by a PI fraction from a Li-EDA treatment, appeared to be altered to a minimum extent. No obvious explanation for these observations emerges since the active species in Li-EDA reduction and electrolytic reduction has been inferred to be the same (*7*).

ACKNOWLEDGMENT

The support of the American Petroleum Institute, Project 56, is gratefully acknowledged. C, H, N, S, and ash determinations were made by K. W. Zimmerman, University of Melbourne, Australia.

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RECEIVED for review August 17, 1964. Accepted February 10, 1965. A portion of this article is taken from J.F. Branthaver's Ph.D. thesis, University of Utah, Salt Lake City, Utah.