OXYGEN COMPOUNDS AND PORPHYRINS IN SOME LOCAL CRUDE OILS

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BY

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CHAPTER I

INTRODUCTION

INTRODUCTION

Evaluation of both porphyrins and oxygen compounds (fatty acids, naphthenic acids and phenols) is very important to obtain informations about origin and migration of crude petroleum. Moreover, their distribution permits applications to geologic problems. The presence of porphyrins in crude oil shows the transformation of organic matters into petroleum.

1.1 PORPHYRINS

The porphin nucleus consists of four "pyrrole type" rings joined by four methine bridges giving cyclic tetrapyrrole structure (Fig. 1) which was the parent system suggested by Kuster$^{(1)}$. In 1912, Fischer$^{(2)}$, the father of contemporary porphyrin chemistry, did have a band in the final proof, which was provided by his total synthesis of protoheme

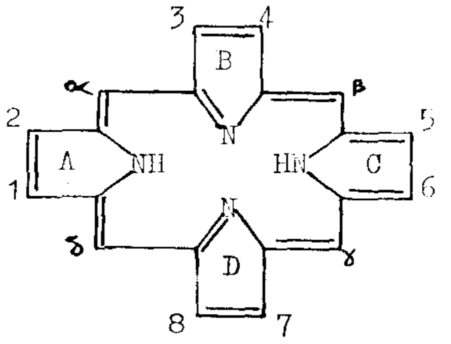

Fig. 1: Structure of porphin.

From porphin, the porphyrins are formally derived by substitution of some or all of the peripheral positions with various side-chains groups. In the classical system of nomenclature, the **peripheral** positions are numbered from 1 to 8 (c.f. Fig. 1) and the"interpyrrolic" methine positions usually termed "meso" are designed α , β , γ and δ . The rings are usually lettered A,B,C and D(3).

Two closely related classes of tetrapyrrole compounds are the dihydroporphyrins and the tetrahydroporphyrins. The dihydroporphyrins are commonly known as chlorin include two "extra" hydrogen atoms on one of the pyrrole rings, saturating one of the double bonds thus impairing the resonance stability of the porphyrin structure by interfering with conjugated band system. The tetrahydroporphyrins carry four "extra" hydrogen atoms. As would be expected, the resonance stability is further impaired. The corresponding chlorin and tetrahydroporphyrin structures are as in Figs. 2a and 2b.

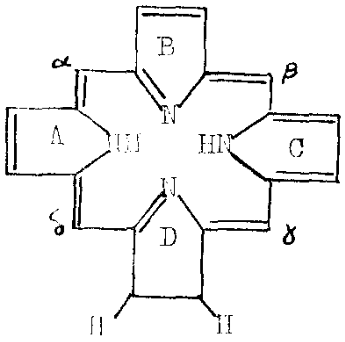

Fig. 2a: Structure of chlorin.

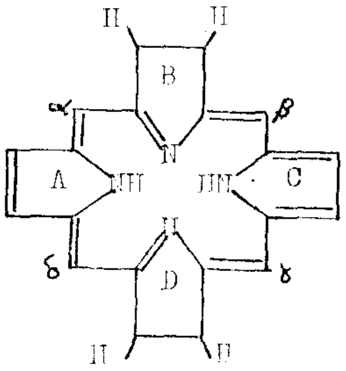

Fig. 2b: Structure of tetrahydroporphyrin.

The structure and properties of porphyrins and metalloporphyrin complexes depend on the basic porphyrin nucleus and groups in peripheral positions of this nucleus, as recently and comprehensively reviewed by Flak(4).

1.1.1 Porphyrins In Petroleum (Petroporphyrins)

Porphyrins in petroleum and bitumens were recognized by Treibs(5) in 1934. He isolated and identified the major of metalloporphyrins, vanadyl deoxophylloerythroetioporphyrin (DPEP) in petroleum and shale. Treibs realized that identification of these pigments proved that petroleum was derived from plant and animal organic remains and, thus, explained the origin of petroleum. A series of reactions postulated by Treibs described how the chlorophylls of green plants, the starting materials were converted to metalloporphyrin, the end product found in petroleum. From this beginning, the science which is today called "organic geochemistry" developed.

Based on Treibs observation, a major concept of this field was put forward, that of "biological marker". These are compounds in which a sufficient part of the carbon skelton is preserved after having undergone accumulation and diagenesis, that can be still correlated with the original biological precursor. Triebs explicity denoted chlorophyll and vanadyl porphyrin as such a precursor-fossil pair. The full impact of this concept was not realised untill it was extended to other classes of organic compounds. This definition of "chemical fossil" and "biological marker" was presented, more fully explained and illustrated in 1967 by Eglinton *et.al*(6).

Several key points in the understanding and development of porphyrin geochemistry followed Treibs pioneer finding. Identification of a second metallochelate and , to date, the only other recognized metallogeoporphyrin, nickel porphyrin, by Glebovskaia *et. al.*(7) in 1948 encouraged further investigations. The extent of the diagenetic realm was only beginning to be understood when Corwin(8) in 1959 pointed out the complexity of the geoporphyrin system. He recognized that porphyrins present in petroleum were different from so called natural porphyrins and, for that reason, the term "petroporphyrins" was coined by him. Corwin(9) explained that the petroporphyrins were neither biochemically derived porphyrins. In 1966, Baker(10) analyzed a suite of petroporphyrins by mass spectrometry and provided proof that they were as complex as Corwine had suspected. Characterization was greatly enhanced by synthesis and crystal structure determination of vanadyl DPEP reported by Baker(10-12). Understanding of the complexity of this group of naturally occuring compounds took another jump by Blumer(13) in 1970. He had concentrated porphyrins of molecular weight of more than 1000 and had indications of fossil porphyrins of up to 20000 mole. wt.

Migal *et. al.*(14) extracted vanadyl and nickel porphyrine complexes in butemens and petroleum of Moldavia and estimated their distribution. They found that the concentration of nickel and vanadyl porphyrin complexes were (2.5-5.9) x 10^{-2} and (1.5-7.5) x 10^{-2} mg/100g bitumene, respectively.

Distribution of porphyrins in the oil and bitumines of Kama Revier region was investigated by Demenkova *et. al.*(15).

Sobolev *et. al.*(16) carried out the evaluation of petroleum in the eastern part of the Caspin Syncline (USSR). They compared the geochemical data for two regions:

i- Upper Carboniferous (Ostansuk Field) petroleum yeilding almost no gasoline fraction and containing only nickel porphyrin complexes.

ii-Lower Permain (Kenkiyak and Kumsai Fields) petroleum containing only vanadyl porphyrin complexes having lower density and viscosity and higher content of cyclic structure than the former.

Porphyrins in petroleums of the Sangachaly Sea and Duvannyi Sea Field (USSR) were estimated by Baboev(17). It was found that the petroleums contained 0.55-1.09 mg of Ni porphyrin complexes per 100 g but no vanadyl porphyrin. The content increased with depth. The presence of porphyrins showed the genetic connection between the organic substance and petroleum.

Sedymova *et. al.*(18) investigated the distribution of the porphyrin-V-complex(I) and porphyrin-Ni-complex(II) in petroleum in the centeral part of Weastern Siberian (USSR). The distribution of I and II is related to the depth, asphaltene content and concentration of carbonyl groups. In all samples studied, the amount of I is greater than that of II and the concentration of both were directly related to the concentration of both asphaltene and inversly related to the concentration of carbonyl groups.

Vanadyl porphyrin complexes were detected in petroleum of the Volgograd Region (USSR) by Zulfugarly et. al.(19). It was found that the content of the complexes decreases with increasing depth of the petroleum deposit, the relation being especially observed at depth 1800 m. The concentration of the vanadyl complexes was correlated with composition and structure of the petroleum hydrocarbons. Only an insignificant part of nitrogen, vanadium and probably nickel of the petroleum was connected with the metalloporphyrin complexes. Nickel porphyrin complexes were not detected in the petroleum under investigation.

Distribution of metalloporphyrin complexes and simple pyrrole compounds in petroleums and bitumens of Weastern Kajakhstan (USSR) was estimated by Bakinova et. al.(20). Most of the petroleums contained only V-porphyrin complexes. Petroleums occuring below the salt-bearing horizon also contained Ni-porphyrin complexes. The content of V-porphyrine complexes increased as the depth of petroleum formation and sulfur content of the petroleum increased. Indole and pyrrole were only the pyrrole-type compounds found in the petroleums. The metalloporphyrins were concentrated in the petroleum bitumens.

Lakatos *et. al.*(21) estimated the porphyrin content of characteristic Hungarian crude oils. It was found that the content of porphyrin is related to geochemical classification of liquid hydrocarbons occuring in the Pannonian basin. Experimental results showed that the petroleum samples investigated contain, exclusively, nickel and vanadyl porphyrins at very different concentrations (1-127 ppm). The petroleum samples from Nagylengyel has the highest porphyrin content (127 ppm). Porphyrins isolated comprise both etio and phyllo types, however, the presence of chlorines or of metal complexes other than those mentioned above could not be detected in the Hungarian crude oils.

The content and distribution of metalloporphyrins of various petroleums were studied(22). The usual content of metalloporphyrins of petroleum was 1-2 mg/100 g petroleum . The most common were vanadyl porphyrins. The content of vanadyl and nickel porphyrins are not correlated with the petroleum composition.

The relation between the content of metalloporphyrins of the Tartory petroleums and their composition and properties was studied by Kurbsku *et. al.*(23). It was found that the main metalloporphyrins were vanadyl porphyrins and trace of nickel porphyrins were found in some petroleums. The content of metalloporphyrins of petroleum increases as its content of sulfur and asphaltene increased.

The role of porphyrins in the formation of petroleum has been studied by Babaev et. al.(24). It was found that the petroleums under investigation contain nickel but not vanadyl porphyrins. The concentration of the nickel porphyrins increases with the depth of the deposition. The change in concentration and composition is attributed to the adsorption of the high molecular weight components of petroleum and the associated metallocomplexes during migration of petroleum to the upper harisons, rather than to the formation of new products. The porphyrins are formed by the interaction of the pigments of the initial organisms with the other chemical compounds in the system during the period of accumulation and transformation of organic matter into petroleum.

1.1.2 Extraction of Porphyrins From Petroleum Products

The porphyrins in bitumens are present predominantly as vanadyl and nickel chelates. These chelates are in many of their physical properties very similar to the materials with which they are associated in the bitumens, petroleum or sediments. For this reson, there is no single method of isolation suitable for all cases. The most common and convenient method is extraction by strong acids, but it has the disadvantage that the distinction between the porphyrins chelated with nickel and those chelated with vanadium is lost. Other methods such as adsorption chromatography, solvent extraction and gel permeation chromatography preserve the metallochelates for the study. It should be noted that the recovery of porphyrin by these procedures is not quantitative and all probably discriminate against the carboxylic