# SEPARATION AND CHARACTERIZATION OF VANADYLPORPHYRINS FROM ROMASHKINO PETROLEUM

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A combination of extraction and adsorption chromatography was employed for the separation of vanadylporphyrins present in the asphalt of the petroleum from the locality Romashkino (U.S.S.R.). Mass spectrometric analysis revealed that the vanadylporphyrin concentrates contained alkylporphyrins of the etio type and monocycloalkanoalkylporphyrins of the deoxophylloerythroetio type, in both cases with 27—36 carbon atoms in the molecule, and alkylbenzoporphyrins of the rhodo I type with 30—36 carbon atoms in the molecule. The etio type was established to be the predominant porphyrin type.

The view upon the nature of the bonding of vanadium in petroleum and some petroleum products has undergone changes in the past. The original hypothesis that vanadium occurs in petroleum asphaltenes in the form of inorganic salt crystals[1] was later controverted by the detection of vanadium porphyrins in various sorts of crude oils, asphalts, oil shales, and ozokerites from different deposits[2-4]. Garner and coworkers[5] and later also other authors[6,7] found that in addition to porphyrins, vanadium was bonded in petroleum also in the form of other organic compounds. From an analysis of the electron spin resonance spectra of many petroleum and petroleum fraction samples, and from all the other state-of-the-art information on the nature of the vanadium bonding in petroleum it could be concluded that vanadium occurs exclusively in the form of organometallic complexes of $VO^{2+}$ ions[8,9], of porphyrinic or non-porphyrinic nature[9,10-14].

For a study of petroleum vanadylporphyrins, the way of their separation or preparation of the corresponding concentrates, suitable for their characterization, is of great importance. For this purpose are usually employed extraction methods[15] or various types of chromatographic techniques (adsorption[16,17], thin layer[18], paper[19], or gel[11,20,21] chromatography).

For the characterization of the petroleum compounds of vanadium, spectral methods — particularly near UV-VIS absorption spectrophotometry[2-4,18], mass spectrometry[9,22,23], and electron spin resonance[9,24] — proved to be well suited.

In the present work, some of the mentioned instrumental techniques were employed for a characterization of the vanadylporphyrins present in the imported petroleum from the locality Romashkino (U.S.S.R.) in order to gain detailed information on these compounds, especially with regard to the catalytic treatment of this raw material.

## EXPERIMENTAL

### Preparation of Vanadylporphyrin Concentrate

As the starting material served the asphalt from the Romashkino petroleum prepared by propane deasphalting (the industrial sample taken at the Paramo Works, Pardubice, in 1969 was obtained by deasphalting a 25% distillation residue; the asphalt was prepared in a 65% yield with respect to this residue). From this asphalt, asphaltenes were first extracted with n-pentane, and their acetone and acetonitrile extracts were then obtained as reported previously[21].

The vanadylporphyrins were then separated by means of adsorption chromatography. Silica gel and alumina (Lachema, grain size 100—200 μm) served as the adsorbents for column chromatography. The separation was performed in glass columns with the ends equipped with brass closures attached to the column by screw joints with silicone rubber gaskets. The inner diameter of the columns was 10 mm, length 700 mm for chromatography on silica gel and 200 mm for chromatography on alumina. n-Heptane, benzene, and acetone (all reagent grade purity) served as the eluents; their flow rate, 40 ml/h and 15 ml/h for the 700 and 200 mm columns, respectively, was provided by a micropump MC-300 (Mikrotechna) connected to the column *via* a Teflon capillary, i.d. 0·7 mm.

The acetone and acetonitrile extracts of the asphaltenes were first chromatographically treated on silica gel deactivated with 10% wt. water. In both cases, 0·4 g of the sample dissolved in benzene was injected. The elution was carried out by applying mixtures n-heptane–benzene (1 : 1 vol.), benzene–acetone (9 : 1 vol.), and benzene–methanol (1 : 1 vol.). in this order. The vanadylporphyrins were eluted by the mixture benzene–acetone as a sharp-edge deep red band. For an additional increase of the vanadium (vanadylporphyrin) content, the vanadylporphyrin fractions from the silica gel were chromatographed on neutral alumina deactivated with 8% wt. water. 0·03 g of the sample dissolved in benzene was injected; the non-porphyrinic moiety was washed out with benzene, the vanadylporphyrins were then eluted with the mixture benzene–acetone as a sharp-edge bright red band. In this manner were for both extracts successively treated the vanadylporphyrin fractions obtained by chromatography of the extracts on silica gel, the corresponding vanadylporphyrin fractions from alumina were combined and the resulting vanadylporphyrin concentrates were employed for a characterization by the methods of instrumental analysis.

### Absorption Spectrophotometry in the Near Ultraviolet — Visible Region

The measurements were performed on an absorption spectrophotometer Pye Unicam SP 800 B. The vanadylporphyrin concentrates were characterized by their electronic absorption spectra measured in the region 350—650 nm for benzene solutions. The content of the metaloporphyrins was determined by the method suggested by Sugihara and Bean[25], consisting in the graphical integration of the characteristic so-called Soret absorption band at 400 nm, using the integral absorptivity of vanadyletioporphyrin I (the value $4{\cdot}84 \,.\, 10^6$ l nm $\text{mol}^{-1}$ $\text{cm}^{-1}$ ($4{\cdot}84 \,.\, 10^{-4}$ $\text{m}^3 \,.\, \text{mol}^{-1}$) was found for benzene as the solvent).

### Atomic Absorption Spectroscopy

The measurements were performed on a flame atomic absorption spectrometer Varian Techtron AA6, equipped with a burner AB-50 for the applied dinitrogen oxide–acetylene flame. As the source of radiation served an ASL shielded high-intensity hollow cathode lamp for vanadium. The determination parameters were as follows: analytical line 318·4 nm, spectral slit width 0·2 nm, discharge lamp current 20 mA, flow rates of the oxidant and of the fuel 190 and 82 $cm^3 s^{-1}$, respectively, observation height 0·2 cm, solution aspiration rate 33 $cm^3 s^{-1}$. The content of vanadium in the vanadylporphyrin concentrates was determined in xylene solutions by applying the calibration curve method; vanadyltetraphenylporphyrin[26] served for the preparation of the reference solution of vanadium in xylene.

### Mass Spectrometry

For a detailed characterization of the vanadylporphyrin concentrates, the mass spectra were measured on a spectrometer AEI Model MS 9. The direct inlet technique was applied. The spectra were run at the sample evaporation temperature 230—340°C, temperature of the source was 230°C, ionizing electron energy 70 eV. The mass scale was calibrated by means of perfluorotributylamine, the spectra were measured with the resolution 3000 on a 10% valley.

## RESULTS AND DISCUSSION

The separation procedure applied to the acetone and acetonitrile extracts of the Romashkino asphaltenes afforded in both cases approximately 30 mg of the vanadylporphyrin concentrate of relatively high purity with the yields of 0·4 and 0·2%, respectively, with respect to the starting asphalt. The contents of vanadium and vanadylporphyrins were determined in the two vanadylporphyrin concentrates. The results are given in Table I, the contents of these substances in the starting asphalt and in the two extracts are given for a comparison, too.

As follows from the data of Table I, the content of vanadium increased in the concentrates 12 and 9 times, respectively, that of vanadylporphyrin 48 and 35 times, respectively. In both concentrates, 70%, hence the essential part, of the total metal content is porphyrin-bonded, whereas in the extracts it is about 30% and in the starting asphalt as little as 8% only.

TABLE I

Contents of Vanadium and Vanadylporphyrins in Asphalt from Romashkino Petroleum and in the Obtained Concentrates of These Substances

| Sample | Vanadium content | | Vanadylporphyrin content | |
|---|---|---|---|---|
| | ppm | μmol $g^{-1}$ | ppm | μmol $g^{-1}$ |
| Petroleum asphalt | 413 | 8·1 | 815 | 1·5 |
| Acetonitrile extract of the asphaltenes | 756 | 14·8 | 2 772 | 5·1 |
| Concentrate from the acetonitrile extract | 5 086 | 99·8 | 38 823 | 71·4 |
| Acetone extract of the asphaltenes | 695 | 13·6 | 2 337 | 4·3 |
| Concentrate from the acetone extract | 3 892 | 76·4 | 28 762 | 52·9 |

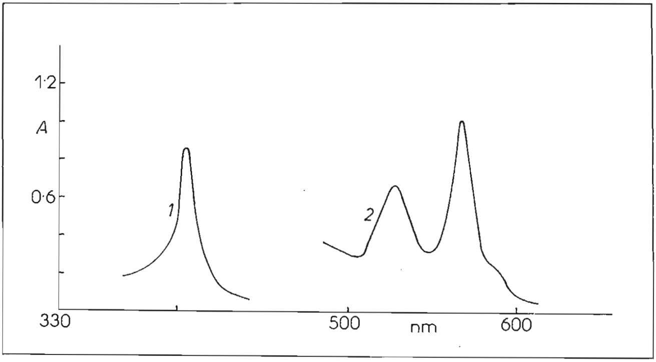

FIG. 1

Electronic Absorption Spectrum of the Vanadylporphyrin Concentrate from the Acetonitrile Extract of the Asphaltenes

Solution in benzene, concentration *1* 2·43 . $10^{-2}$ mg/ml, *2* 4·87 mg/ml.

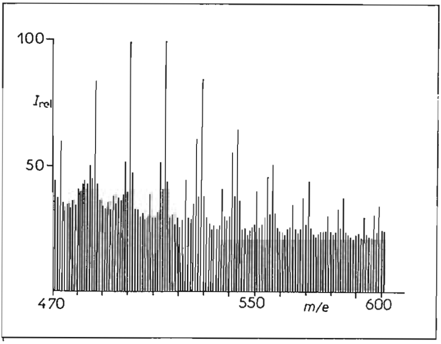

FIG. 2

Mass Spectrum of the Vanadylporphyrin Concentrate from the Acetonitrile Extract of the Asphaltenes

The two vanadylporphyrin concentrates were further characterized by their electronic absorption spectra. Fig. 1 shows as an example the spectrum of the vanadylporphyrin concentrate obtained from the acetonitrile extract of the Romashkino asphaltenes; the other spectra were alike. They feature the characteristic absorption bands of vanadylporphyrins at 407, 530, 570, and 588 nm. The occurrence of the absorption bands at 530 nm and 570 nm and their intensity ratio reveal the presence of two basic types of petroleum porphyrins, namely etio type alkylporphyrins and deoxophylloerythroetio type (DPE) monocycloalkanoalkylporphyrins. The absorption band at 588 nm and its intensity relative to the intensities of the two former bands indicate the presence of a small quantity of rhodo type porphyrins exhibiting the alkylbenzoporphyrin or monocycloalkanoalkylbenzoporphyrin structure.

In order to identify the individual members of the homologous series of the porphyrin types present and to find the predominant porphyrin type, the two concentrates were subjected to mass spectrometric analysis: Fig. 2 shows the mass spectrum of the vanadylporphyrin concentrate obtained from the acetonitrile extract of the asphaltenes.

Ions of the homologous series of the etio type vanadylporphyrins, whose masses obey the relation $M = 375 + 14n$, where $n$ is an integer, and ions of the homologous series of the DPE type vanadylmonocycloalkanoalkylporphyrins, of the masses $M = 373 + 14m$, where $m$ is an integer $m \geqq 2$, were identified in the spectra of both concentrates. The mass spectrum of the vanadylporphyrin concentrate obtained from the acetonitrile extract of the asphaltenes indicates in addition the presence of ions belonging to the homologous series of the rhodo I type vanadylalkylbenzoporphyrins, obeying the relation $M = 425 + 14n$, where $n$ is an integer. In the concentrate from the acetone extract, the rhodoporphyrin ions could not be detected; this can be explained in terms of the lower concentration of this type porphyrins and particularly their lower volatility as compared with the two types found, and probably also the different composition of the non-porphyrin moiety in the two concentrates which affects the course of the sample evaporation.

Table II lists the ions of the homologous series of the porphyrins present, identified in the analyzed concentrates, their intensities relative to the most intense porphyrin ion, *viz.* that of the mass 515, and also the number of the carbon atoms in the saturated substituent of the basic structural unit of porphyrins – porphine. In the case of the etio type alkylporphyrins and DPE type monocycloalkanoalkylporphyrins, this number of the carbon atoms falls within the range 7–16 in both concentrates, in the rhodo I type porphyrins found in the vanadylporphyrin concentrate from the acetonitrile extract of the asphaltenes this number is 6–12. In order to establish the predominating porphyrin type, the ratios $\sum I_{\text{DPE}}/\sum I_{\text{etio}}$ were calculated for the two concentrates; the values 0·71 and 0·50 were obtained for the acetonitrile and and acetone extracts, respectively.

The mass spectrometric measurements revealed that the vanadylporphyrins occurring in the petroleum examined represented a complex multicomponent mixture of porphyrins of various types. In the extractable part of the Romashkino vanadylporphyrins, etio and DPE type porphyrins with 27–36 carbon atoms in the molecule in both cases and rhodo I type porphyrins with 30–36 carbon atoms in the molecule were identified. The etio type was found to prevail. Open remains the question of

TABLE II

Relative Intensities of the Peaks in the Mass Spectra of the Vanadylporphyrin Concentrates

| $m/e$ | $n$(C)[a] | Concentrate from the acetonitrile extract | | | Concentrate from the acetone extract | |
|---|---|---|---|---|---|---|
| | | etio | DPE | rhodo | etio | DPE |
| 471 | 7 | | 43·7 | | | 28·1 |
| 473 | 7 | 60·0 | | | 37·9 | |
| 485 | 8 | | 50·2 | | | 29·5 |
| 487 | 8 | 83·7 | | | 58·1 | |
| 499 | 9 | | 52·1 | | | 30·7 |
| 501 | 9 | 98·5 | | | 92·0 | |
| 509 | 6 | | | 38·9 | | |
| 513 | 10 | | 57·3 | | | 32·1 |
| 515 | 10 | 100·0 | | | 100·0 | |
| 523 | 7 | | | 44·7 | | |
| 527 | 11 | | 60·8 | | | 33·5 |
| 529 | 11 | 85·4 | | | 83·1 | |
| 537 | 8 | | | 41·0 | | |
| 541 | 12 | | 56·1 | | | 32·8 |
| 543 | 12 | 65·3 | | | 57·8 | |
| 551 | 9 | | | 40·2 | | |
| 555 | 13 | | 45·7 | | | 24·1 |
| 557 | 13 | 51·1 | | | 41·5 | |
| 565 | 10 | | | 34·5 | | |
| 569 | 14 | | 37·8 | | | 19·2 |
| 571 | 14 | 43·5 | | | 27·2 | |
| 579 | 11 | | | 30·6 | | |
| 583 | 15 | | 33·2 | | | 18·7 |
| 585 | 15 | 38·2 | | | 23·0 | |
| 597 | 12 | | | 29·5 | | |
| 593 | 16 | | 31·1 | | | 18·5 |
| 599 | 16 | 34·7 | | | 17·3 | |

[a] Number of the carbon atoms in the saturated porphine substituents.

porphyrins of highly aromatic nature, embedded probably in the complex aromatic structure of the heaviest asphaltenic-resinous petroleum fractions. The separation of these compounds has not been so far solved satisfactorily.

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