MICROEXTRACTION OF VANADYL PORPHYRINS AS WATER POLLUTANT BY NANO-BASKETS

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ABSTRACT

Vanadyl porphyrins are present in the produced water of oil fields and are considered as one of the water pollutant groups. The novelties of this approach is nano-extraction of charged porphyrins by nano-baskets of calixcrown, which act as the settling agents as well as the inclusion ligands. Four proton di-ionizable diacid conformers of 25,26-bis(carboxymethoxy)calix[4]arene-27,28-crown-3, -crown-4, -crown-5 and -crown-6 in the cone conformation were synthesized and used. The related parameters including ligand concentration, volume of water disperser, salt effect and extraction time were optimized. The linear range, detection limit (S/N = 3) and precision (RSD, n = 6) were determined to be 0.2–50, 0.07 μgL−1 and 5.3% respectively. The established method was applied to determine the target compound in five samples of live crude oil were sampled from an Iranian offshore field. Owing to the overall differences (such as organic media, inclusion extraction water-soluble ligands, etc) the comparison of the proposed method with the traditional liquid-liquid microextraction was inapplicable. These results revealed that the new approach is competitive analytical tool and an alternative of the traditional methods in the crude oil and related systems.

Key Words: Nano-baskets, Liquid-Liquid Microextraction, Vanadyl Porphyrins, Calixcrown, Crude oil

INTRODUCTION

Determination of metalloporphyrins in crude oil is of interest in understanding the geochemical origins of petroleum reservoirs, the diagenetic and the catagenetic pathways in the oil formation and the maturation, depositional and environmental reconstruction studies. Alfred Treibs discovered the petroleum porphyrins (petroporphyrins) in 1934. Vanadyl porphyrins were the first petroleum biomarkers and they are molecular fossils of tetrapyrrolic pigments such as bacteriochlorophylls and chlorophylls. Vanadium in crude oil causes corrosion problems that derive from the formation (in the combustion chamber of power plants) of sodium vanadates (with low melting point), which react with the metal surface of the superheaters and form the metal oxide.

According to the literature reports, five main types of porphyrins along with their homologues are present in crude oil including Etioporphyrins (Etio), Deoxophylleerythroetio porphyrin (DPEP), Tetrahydrobenzo DPEP, benzo-Etio and benzo-DPEP. Fig. 1 illustrates the chemical structure of above-mentioned scaffolds. New sample-preparation methods, which are easy to use, inexpensive, fast, environmental friendly and compatible with a range of analytical instruments, are outspreaded. More recently, efforts have been placed on the development of the Dispersive Liquid–Liquid Microextraction (DLLME) procedure, which is based on a ternary component solvent system. The dispersion of extraction solvent by disperser solvent within the aqueous solution leads a large contact area between the aqueous phase and the extraction solvent.

Flocculation, which is the first action of the demulsifier on an emulsion, involves the joining of the small water droplets. When magnified, the flocks take on the appearance of fish-egg bunches. If the emulsifier film surrounding the water droplets is very weak, it will break under this flocculation force and the coalescence, which is the rupturing of the emulsifier film and the uniting of water droplets, will take place without further chemical action. Once the

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coalescence begins, the water droplets grow large enough to settle out.

Asphaltenes are the high polar fraction of the petroleum and play an important role in the formation and stabilization of the water in crude oil emulsions. The goal of demulsifier action is to offset the stabilization of emulsion both from the kinetic and thermodynamic points of view. Demulsifiers are molecules that aid the separation of water from oil and prevent formation of water in oil mixture. Some demulsifiers are polymers, others have calixarene and calixcrown structures. Calixarenes and calixcrowns have been subjected to extensive researches and reviews in development of extractants, transporters, stationary phases, electrode ionophores, optical sensors and medical researches over the past decades.

Fig. 1: Chemical structure of five main types of Vanadyl Porphyrins

AIMS AND OBJECTIVES

In this paper, a novel approach, entitled self-settled dispersive liquid phase microextraction, was introduced and is used for determination of vanadium porphyrins in live crude oil. The main objectives of this work are applicability of water as disperser phase, removing the centrifuging step, settling the water dispersed droplets by calixcrowns, conducting the dispersive liquid phase microextraction in complex organic systems and inclusion microextraction of charged porphyrins by ionizable calixcrowns. This method deals with twin role of calixcrowns scaffolds as the settling and the complexing agent.

MATERIAL AND METHODS

Doubly distilled and Deionized water (DDW) with a specific resistivity of 18 MΩcm, from a Milli-Q water purification system (Millipore, Bedford, MA) was used as disperser. According to the literature methods, the vanadyl porphyrins were separated from the oil matrix and were used as standard solutions. The oil samples were collected from one of the Iranian offshore oil fields and their chemical characteristics are presented in Table 1.

Synthesis of intermediates

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Acetonitrile (MeCN) was dried over CaH₂ and distilled immediately before use. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use. Cs₂CO₃ was activated by heating at 150 ºC overnight under high vacuum and stored in a desiccator. Melting points were determined with a Mel-Temp melting point apparatus. Infrared (IR) spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrometer as deposits from CH₂Cl₂ solution on NaCl plates. The ¹H and ¹³C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR (¹H 500 MHz and ¹³C 126 MHz) spectrometer in CDCl₃ with Me₄Si as internal standard unless mentioned otherwise. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constants (J) values are in Hz. The synthesis scheme for preparation of cone p-tert-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (10-13) are presented in Fig. 2.
Table 1: Chemical characteristics of the blend crude oil used in the experiments

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<th>Component</th>
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<th>Flashed gas (mol %)</th>
<th>Flashed liquid (mol %)</th>
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Fig. 2: Synthesis of cone \( p \)-tert-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6

**Apparatus**

The extractions and injections were performed by microsyringe (Agilent, CA, USA) bearing an angledcut needle tip (needle id: 0.11 mm and glass barrel id: 0.6 mm). Atomic absorption spectrometer of Shimadzu (model AA-670G) with deuterium lamp background correction and a graphite furnace atomizer (GFA-4B) was used. A reversed phase (RP) C₁₈ column (4.6mm diameter, 100 mm length, 2 μm macropore size and 13 nm mesopore size) was obtained from Merck (Darmstadt, Germany). A RP-C₁₈ guard column was fitted upstream of the analytical column. The mobile phase was optimized to be...
45:55, v/v methanol–water and was delivered by an HPLC pump (Waters LC-600). The UV detection wavelength was set at 254 nm and the flow rate of the mobile phase was adjusted to be 3 ml/min.

Sample preparation
5.0 mL pre-washed crude oil was placed into a 10-mL screw-cap glass centrifuge tube with conic bottom. 100.0 μL of distilled water (as dispersive solvent) containing 0.001 g calixcrown (as extraction ligand) was rapidly transferred into the above-mentioned centrifuge tube and was gently shaken. The calixcrown demulsifier caused the dispersed fine droplets of the extraction phase be sedimented at the bottom of the conical test tube. The volume of the sedimented phase was determined using a 50.0 μL microsyringe and was completely transferred to another 100 μL centrifuge tube. After evaporation of the water under a gentle nitrogen flow, the residue was redissolved in 25 μL LC-grade methanol and injected into HPLC for analysis.

RESULTS AND DISCUSSION
The effects of all parameters (that can probably influence the performance of extraction) were investigated. They were (1) the concentration of demulsifier or extraction ligand (calixcrown), (2) the volume of disperser (water), (3) the extraction time and (4) the salt addition that were investigated and optimized in order to achieve the higher enrichment factor and recovery of vanadyl porphyrins from the samples of live oil.

Effect of the calixcrown concentration
In order to evaluate the effect of calixcrown concentration on the extraction efficiency and the separation of phases, the following experiments were performed using 0.50 ml DDW containing different concentrations of calixcrown (9.5, 14.5, 19.5 and 24.5 mgL\(^{-1}\)). Fig. 3 to Fig. 5 depicts the traces of recovery of vanadyl porphyrins, enrichment factor and volume of sedimented phase versus the calixcrown concentration, respectively.

As illustrated in Fig. 5, the extraction recovery is almost increasing (from 62.0–95.5%) owing to the quantity extraction and high distribution coefficient of vanadyl porphyrins in the conditions of high concentration. Obviously, in Fig. 4, the enrichment factor decreases from 880 to 200. Thus, 10 μL of vanadyl porphyrins was selected in order to obtain high enrichment factor and hence low detection limit and high recovery. According to Fig. 5, by increasing the calixcrown concentration from 10 to 26 mgL\(^{-1}\), the volume of sedimented phase increases (6.0–20.5 μL).

![Fig. 3: Effect of the calixcrown concentration on the recovery of vanadyl porphyrins.](image_url)
Fig. 4: Effect of the calixcrown concentration on the enrichment factor of vanadyl porphyrins. Extraction conditions as with Fig. 3 concentration of calixcrown, 10 mgL\(^{-1}\).

Fig. 5: Effect of the calixcrown concentration on the volume of sedimented phase (N=3). Extraction conditions: as with Fig. 3.

**Effect of the disperser volume**

As discussed above, water was selected as the best disperser solvent, hence, it was necessary to optimize the disperser volume. As a rule, the water disperser (at low volumes) cannot disperse the extracting calixcrown properly. In the other hand, in such conditions, the cloudy solution is not formed completely. For obtaining optimized volume of water, some experiments were conducted using different volumes of water (0.25, 0.5, 1.0, 1.5, 2.0 and 2.5 ml) containing 10.0, 12.5, 16.0, and 24.0 \(\mu\)gL\(^{-1}\) vanadyl porphyrins, respectively. It is necessary to change the volume of vanadyl porphyrins by changing the volume of water in order to obtain constant volume of sedimented phase in all experiments. Fig. 6 illustrates the trace of vanadyl porphyrin's recovery versus the volume of water. Base upon the results, a 0.50 ml water was chosen as the optimum volume of disperser.

**Effect of the extraction time**

The interval time between the injection of the water disperser (containing the extraction ligand)
and starting to decant was defined as the extraction time. The effect of extraction time on the performance of DLLME is a key factor, which is evaluated here. Different extraction times in the range of 0 to 90 min (with constant experimental conditions) were investigated. Based upon the results, the extraction regime is time-independent since an infinitely large surface area is available between the aqueous phase (extraction solvent) and the oil media. According to Fig. 7, this method is very fast and this is a common advantage of DLLME.

![Graph showing extraction recovery (%) vs. volume of water (mL)](image)

**Fig. 6**: Effect of the volume of water disperser on the recovery of vanadyl porphyrins obtained from DLLME (N=3). Extraction conditions as with Fig. 3

![Graph showing peak area (A.U.) vs. extraction time (min)](image)

**Fig. 7**: Effect of extraction time on the peak area of vanadyl porphyrins obtained from DLLME (N=3). Extraction conditions as with Fig. 3

**Effect of the salt addition**

The influence of ionic strength on the performance of DLLME was studied by adding different amounts of NaCl (0–5%), while the other experimental conditions were kept constant. Fig. 8 presents the effect of increasing the ionic strength on the volume of sedimented phase of vanadyl porphyrins. Obviously, by increasing the ionic strength (from 0 to 1%) the volume of sedimented phase decreases and then by more increasing (from 1 to 5%), the volume of sedimented phase increases.
Real sample analysis
The matrix effects on the extraction were also evaluated by studying the applicability of this approach to determine the concentration of vanadyl porphyrins in the crude oil samples taken from one of the Iranian offshore fields. The samples were extracted using DLLME method and analyzed by HPLC–UV. The samples were spiked with vanadyl porphyrin standards at different concentration levels to investigate the matrix effects. A typical chromatogram representing the vanadyl porphyrins is depicted in Fig. 9.

![Graph](image1)

**Fig. 8**: Effect of salt addition on the volume of sedimanted phase obtained from DLLME (N=3). Extraction conditions, as with Fig. 3.

![Graph](image2)

**Fig. 9**: Chromatograms of decanted water and spiked samples at concentration level of 12.5 $\mu$g$\text{L}^{-1}$ vanadyl porphyrins.

**CONCLUSION**
This study introduced a new approach and a self-settled DLLME method combined with HPLC–UV for separation, preconcentration and determination of vanadyl porphyrins in crude oil. This method deals with twin role of calixcrown scaffolds as the self-settling and the complexing agent. Removing the centrifuging step and performing the inclusion microextraction of vanadyl porphyrins by means ionizable calixcrown was the novelty of this project to enhance the preconcentration speed and extraction the vanadyl porphyrins. The results of this study
revealed that the proposed approach is acceptable for preconcentration of vanadyl porphyrins from crude oil samples. The linear range, detection limit (S/N = 3) and precision (RSD, n = 6) were determined to be 0.2–50, 0.07 μgL⁻¹ and 5.3%, respectively.

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REFERENCES


