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ORIGINAL ARTICLE

Extraction of vanadyl porphyrins in crude oil by inclusion dispersive liquid–liquid microextraction and nano-baskets of calixarene

Bahram Mokhtari · Kobra Pourabdollah

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Abstract The novelties of this approach are introducing the self-settled dispersive liquid–liquid microextraction technique to remove the centrifuging step, conducting the dispersive liquid–liquid microextraction in complex organic systems, applicability of water as disperser phase, and inclusion microextraction of charged porphyrins by nano-baskets of calix[4]arenes, which act as the settling agents as well as the inclusion ligands. Diacid *p-tert*-butylcalix[4]arene in the cone conformation was 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 μg L^{-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. Moreover, in those systems that the inclusion separation is not requested, it is possible to use a tertiary system including a proper extraction agent/solvent and calixarene phase, as settling agent, along with the aqueous disperser in the organic systems.

Keywords Nano-basket · Dispersive liquid–liquid microextraction · Vanadyl porphyrins · Calix[4]arene

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B. Mokhtari · K. Pourabdollah (✉)
Department of Chemical Engineering, Shahreza Branch,
Islamic Azad University, Shahreza, Iran
e-mail: pourabdollah@iaush.ac.ir

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 [1–3] and environmental reconstruction studies [4]. Alfred Treibs discovered the petroleum porphyrins (petroporphyrins) in 1934 [5]. Vanadyl porphyrins were the first petroleum biomarkers [6] and they are molecular fossils of tetrapyrrolic pigments such as bacteriochlorophylls and chlorophylls [7]. 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 [8].

According to the literature reports [4, 9, 10], five main types of porphyrins along with their homologues are present in crude oil including etioporphyrins (Etio), deoxophylleoerythroetioporphyrin (DPEP), tetrahydrobenzo DPEP, benzo-Etio and benzo-DPEP. Figure 1 illustrates the chemical structure of above-mentioned scaffolds.

Up to 30% of vanadium and 25% of nickel in Tatarstan crude oil are found as porphyrin complexes. Ion et al. [11] analyzed the vanadyl porphyrin distribution of Romanian petroleogenetic rocks by UV–Vis spectrophotometry, FTIR, ICP-atomic emission spectrometry, ESR and X-ray fluorescence spectroscopy. Holden and coworkers [7] developed the method of high-resolution reflectance spectroscopy for determination of porphyrins (low levels) in the kerogen fraction. After that, Premovic et al. [12, 13] used the electron spin resonance (ESR) to quantify the high levels of vanadyl porphyrins in kerogens.

Saitoh et al. [14] used a series of preliminary separation procedures for preconcentration of metalloporphyrins and

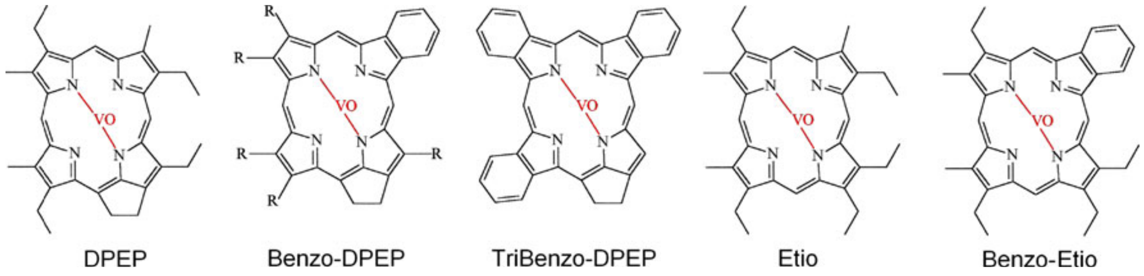

Fig. 1 Chemical structure of five main types of vanadyl porphyrins

determination by reversed-phase high-performance liquid chromatography (HPLC). Ali et al. [4] extracted the nickel and vanadyl porphyrins in residue of Saudi Arabian Crude Oils. The nickel porphyrins were separated from vanadyl porphyrins using adsorption chromatography on alumina and silica gel by solvents of increasing polarity. They monitored the chromatographic separation by UV–Vis spectrophotometry.

New aspects of analytical chemistry in crude oil and reservoir engineering are summarized mainly as chemometrics [15–18], sample preparation and microextraction [19, 20] techniques.

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) [21] 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. Other examples of sample preparation by DLLME have been presented for trace determination of pesticides in soils [22], organophosphorus pesticides in water [23, 24], nickel [25] and Cu(II) [26] in water, and chlorobenzenes in water [27].

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 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 [28]. The goal of demulsifier action is to offset the stabilization of emulsion both from the kinetic and thermodynamic points of view [29].

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 structures. Nano-baskets have been subjected to extensive researches (using gas chromatograph, Teif Gostar Faraz Co.) [30–35] and reviews [36–46] in development of extractants, transporters, stationary phases, electrode ionophores, optical sensors and medical researches over the past decades.

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 calix[4]arenes, conducting the dispersive liquid phase microextraction in complex organic systems, and inclusion microextraction of charged porphyrins by ionizable calix[4]arenes. This method deals with twin role of calixarene scaffolds as the settling and the complexing agent.

Experimental procedure

Materials

Doubly distilled 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 [4, 9], 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 diacid *p*-*tert*-Butylcalix[4]arene (**4**)

n-propyl *p*-toluensulfonate (12.85 g, 60.0 mmol) and K_2CO_3 (82.93 g, 600 mmol) were added to the suspension of the *p*-*tert*-butylcalix[4]arene **1** (19.46 g, 30.0 mmol) in dry *n*-C_3H_7CN (200 mL). The reaction mixture was

Table 1 Chemical characteristics of the blend crude oil used in the experiments

Component	Stream liquid (mol%)	Flashed gas (mol%)	Flashed liquid (mol%)
N_2	00.04	00.31	00.00
CO_2	00.35	02.78	00.00
H_2S	00.57	04.52	00.00
CH_4	03.76	30.14	00.00
C_2H_6	01.50	12.02	00.00
C_3H_8	03.77	21.90	01.18
i-C_4H_{10}	01.92	07.25	01.16
n-C_4H_{10}	07.23	12.40	06.49
i-C_5H_{12}	02.79	03.21	02.73
n-C_5H_{12}	03.80	02.81	03.94
C_6	07.30	01.86	08.08
C_7	08.76	00.68	09.91
C_8	09.61	00.12	10.97
C_9	08.77	00.00	10.02
C_{10}	06.75	00.00	07.71
C_{11}	03.60	00.00	04.12
C_{12+}	29.48	00.00	33.69
Total sulfur			00.85/mass%
Asphaltenes			00.32/mass%
Waxes			05.00/mass%

refluxed for 20 h and then another portion of *n*-propyl *p*-toluenesulfonate (6.43 g, 30.0 mmol) was added. The mixture was heated for another 20 h. After cooling, the reaction mixture was filtered and the solvent was evaporated in vacuo. The residue was partitioned between CH_2Cl_2 (200 mL) and HCl (1 N, 200 mL). The organic layer was separated, washed with water and evaporated in vacuo. The crude product was purified by chromatography on silica gel column with CH_2Cl_2–hexanes (20:1) as eluent to give 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-26,28-di(1-propoxy)calix[4]arene **2** (88%) as a white solid. The product was recrystallized from *n*-C_3H_7OH-CH_2Cl_2 in 71% yield; mp 240–242 °C; ν_{max} (film)/cm^{-1}: 3800–3200 (OH), 1010 (C–O); ^{1}H NMR ($CDCl_3$): δ 0.99 (s, 18H), 1.06 (t, $J = 7.45$, 6H), 1.27 (s, 18H), 1.75 (m, 4 H), 3.33 (d, $J = 12.94$, 4H), 3.97 (t, $J = 6.47$, 4H), 4.30 (d, $J = 12.82$, 4H), 6.84 (s, 4H), 7.03 (s, 4H), 7.85 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ_c 150.18, 150.30, 146.46, 141.12, 132.88, 127.57, 125.44, 125.30, 33.59, 33.87, 32.12, 31.86, 31.70; Anal. Calc. $C_{50}H_{68}O_4$: C, 78.90; H, 9.00; Found: C, 79.10; H, 9.26.

10 mmol 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-26,28-di(1-propoxy)calix[4]arene **2** was added to the suspension of sodium NaH (0.96 g, 40 mmol) in DMF (100 mL), and the mixture was stirred at room temperature. Once the evolution of hydrogen ceased, a solution of ethyl bromoacetate (22 mmol) in DMF (10 mL) was added over a period of 30 min. The mixture was stirred for 3 h, and another portion of ethyl bromoacetate (10 mmol) in DMF (5 mL) was added. The reaction mixture was stirred for another 2 h and the excess of NaH was carefully decomposed by dropwise addition of water. The mixture was diluted with HCl (1 N, 200 mL) and was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic extracts were washed with water, dried over $MgSO_4$ and evaporated in vacuo. The DMF and the unreacted ethyl bromoacetate were removed by distillation under vacuum (60 °C, 1 mm Hg). The residual pale-yellow oil was purified by chromatography on silica gel with hexanes-EtOAc (40:1) as eluent to give the final products 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-di(1-propoxy)calix[4]arene **3** in 80% yield as a white solid; mp 108–110 °C; ν_{max} (film)/cm^{-1}: 1758 (C=O); ^{1}H NMR ($CDCl_3$): δ_H 0.80 (br s, 9H), 1.04 (br s, 9H), 1.26 (t, $J = 7.20$, 6H), 1.34 (br d, $J = 24.78$, 18H), 2.16 (t, $J = 8.60$, 6H), 2.99–5.08 (m, 24H, $ArCH_2Ar$, OCH_2CO_2, and CH_2), 6.58–7.24 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$): δ_C 173.61, 155.95, 153.39, 153.03, 145.92, 143.49, 135.68, 133.93, 132.23, 131.80, 131.55, 127.26, 125.98, 125.33, 124.79, 124.18, 74.16, 72.95, 60.35, 34.09, 33.57, 31.69, 31.22, 26.07; Anal. Calc. $C_{58}H_{80}O_8$: C, 76.95; H, 8.91; Found: C, 77.08; H, 8.79.

A solution of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-di(1-propoxy)calix[4]arene **3** (5.0 mmol), THF (150 mL) and 10% aqueous Me_4NOH (150 mL) was refluxed overnight. The reaction mixture was acidified with HCl (10%) to pH $\sim$ 1. The solvent was removed in vacuo and CH_2Cl_2 (200 mL) was added. The organic layer was washed with water, dried over $MgSO_4$ and evaporated in vacuo to give the final product 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)-26,28-di(1-propoxy)calix[4]arene **4** in 96% yield as a white solid; mp 252–254 °C; ν_{max} (film)/cm^{-1}: 3320–2410 (CO_2H), 1712 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.60–1.60 (br m, 36H), 2.10–4.16 (br m, 30H), 6.35–4.60 (br m, 8H); ^{13}C NMR ($CDCl_3$): δ_C 180.60, 144.32, 131.88, 125.73, 34.01, 33.95, 31.86, 31.45, 31.12, 29.96, 25.29; Anal. Calcd. $C_{54}H_{72}O_8{\cdot}0.6\,CH_2Cl_2$: C, 72.88; H, 8.20; Found: C, 72.74; H, 7.95.

2.40 mmol 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)-26,28-di(1-propoxy)calix[4]arene **4** was dried by benzene-azeotropic distillation. Oxalyl chloride (3.04 g, 24.0 mmol) was added to the solution and the reaction mixture was refluxed for 5 h under nitrogen atmosphere. The solvent was removed in vacuo to provide the corresponding acid chloride 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(chlorocarboxymethoxy)-26,28-di(1-propoxy)calix[4]arene. Figure 2 illustrated the synthesis procedure of diacid *p-tert*-butylcalix[4]arene **4**.

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) C_{18} column (4.6 mm diameter, 100 mm length, 2 μm macropore size, and 13 nm mesopore size) was obtained from Merck (Darmstadt, Germany). A RP-C_{18} guard column was fitted upstream of the analytical column. The mobile phase was optimized to be 45:55, v/v MeOH–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 diacid *p-tert*-butylcalix[4]arene (as extraction ligand) was rapidly transferred into the above-mentioned centrifuge tube and was gently shaken.

The calixarene 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 re-dissolved in 25 μL LC-grade MeOH 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 (calixarene), (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 calixarene concentration

In order to evaluate the effect of calixarene concentration on the extraction efficiency and the separation of phases, the following experiments were performed using DDW (0.5 mL) containing different concentrations of diacid *p-tert*-butylcalix[4]arene 4 (9.5, 14.5, 19.5 and 24.5 mg L^{-1}). Figures 3, 4, and 5 depicts the traces of recovery of vanadyl porphyrins, enrichment factor and volume of sedimented phase versus the calixarene concentration, respectively.

As illustrated in Fig. 3, the extraction recovery is almost increasing (from 62.0–95.5%) owing to the quantity extraction and high distribution coefficient of vanadyl porphyrins at 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 calixarene

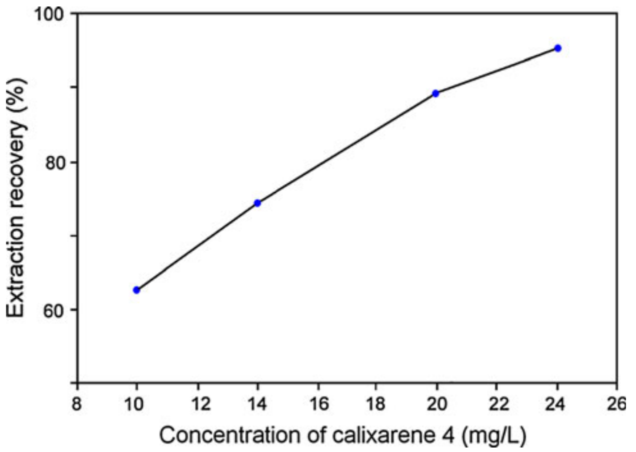

Fig. 3 Effect of the calixarene concentration on the recovery of vanadyl porphyrins. Extraction conditions: oil sample volume, 5.00 mL; disperser solvent (water) volume, 0.50 mL; at ambient temperature

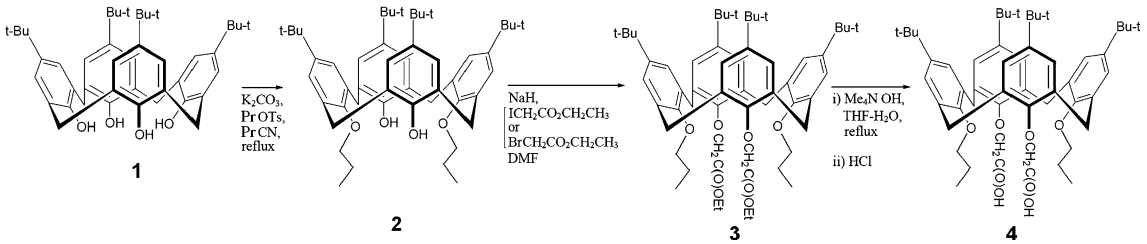

Fig. 2 The synthesis procedure of diacid *p-tert*-butylcalix[4]arene **4** in the cone conformation

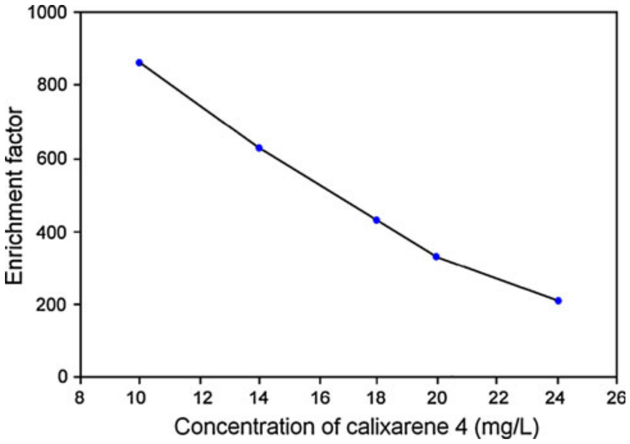

Fig. 4 Effect of the calixarene concentration on the enrichment factor of vanadyl porphyrins. Extraction conditions: as with Fig. 3; concentration of calixarene, 10 mg L^{-1}

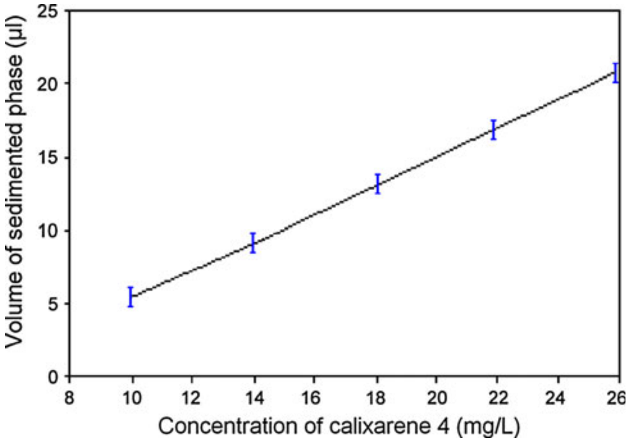

Fig. 5 Effect of the calixarene concentration on the volume of sedimented phase ($N = 3$). Extraction conditions: as with Fig. 3

concentration from 10 to 26 mg L^{-1}, the volume of sedimented phase increases (6.0–20.5 µL).

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 calixarenes 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 µg L^{-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. Figure 6 illustrates the trace of vanadyl porphyrin's recovery versus the volume of water. Base upon the results, water (0.50 mL) was chosen as the optimum volume of disperser.

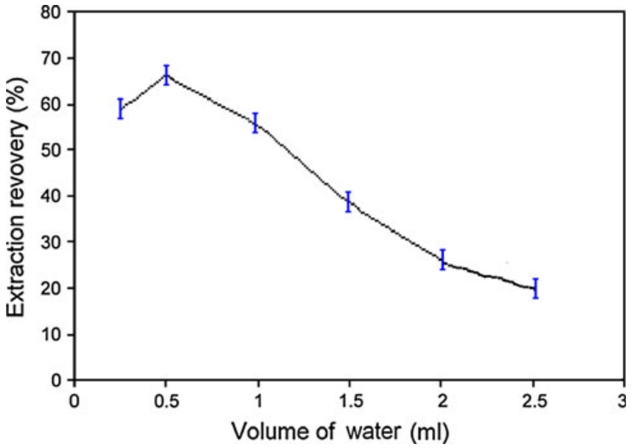

Fig. 6 Effect of the volume of water disperser on the recovery of vanadyl porphyrins obtained from DLLME ($N = 3$). Extraction conditions: as with Fig. 3

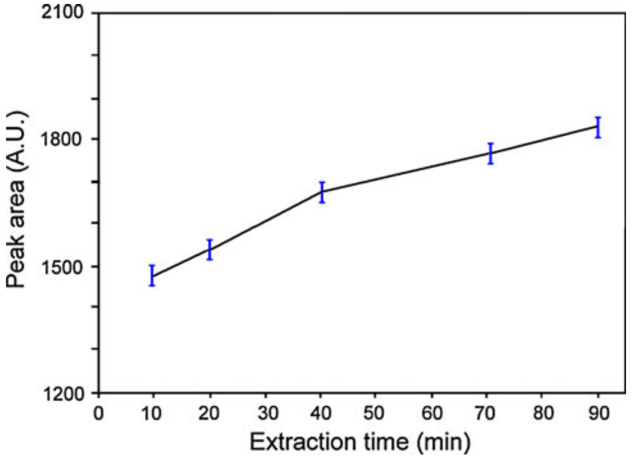

Fig. 7 Effect of extraction time on the peak area of vanadyl porphyrins obtained from DLLME ($N = 3$). Extraction conditions: as with Fig. 3

Effect of the 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. Base 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,

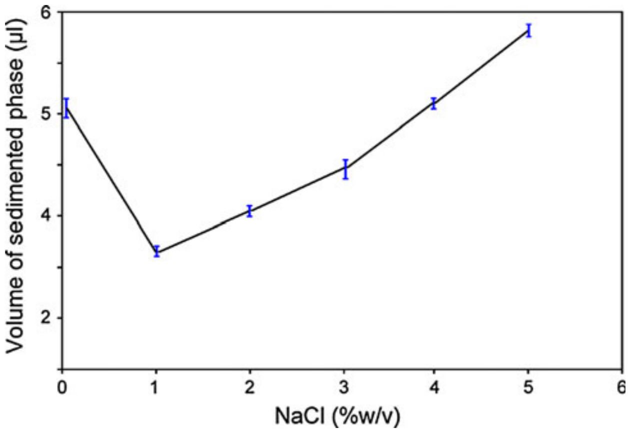

Fig. 8 Effect of salt addition on the volume of sedimented phase obtained from DLLME ($N = 3$). Extraction conditions, as with Fig. 3

this method is very fast and this is a common advantage of DLLME.

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. Figure 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 studding 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.

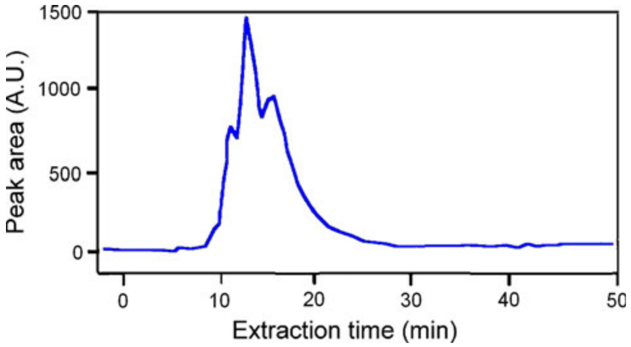

Fig. 9 Chromatograms of decanted water and spiked samples at concentration level of 12.5 µg L^{-1} vanadyl porphyrins

Conclusions

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 calixarene scaffolds as the self-settling and the complexing agent. Removing the centrifuging step and performing the inclusion microextraction of vanadyl porphyrins by means ionizable calix[4]arenes was the novelty of this project to enhance the preconcentration speed and extraction the vanadyl porphyrins. The results 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 µg L^{-1} and 5.3%, respectively.

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