Extraction of petroleum emulsified water and characterization of major ions for the evaluation of its origin

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ABSTRACT

A method for the extraction of emulsified water associated with crude oil was developed, in order to determine the composition of its major cations by inductively coupled plasma optical emission spectrometry (ICP OES) and anions by ion chromatography (IC). The method is suitable to crude oils with water content as low as 0.4% (w/w) and the recovery of elements was satisfactory (80–115%), except in the case of Ba^{2+}, possibly due to the presence of insoluble $BaSO_4$ in the crude oils. Concentrations of dissolved Na^+, Cl^-, Ca^{2+} and Sr^{2+} show good agreement in interlaboratory results of three crude oils and between replicates (0.05–16%), whereas SO_4^{2-} and Ba^{2+} results were more scattered. The emulsified waters had contributions of formation and injection waters and these were reflected in their ions distributions. In the 30 crude oil samples investigated, NaCl was the predominant salt and the correlations of Br^-, Ca^{2+} and Sr^{2+} concentrations to Cl^- concentration showed low values, indicating that the origin of the dissolved ions was through dissolution of halite by rock buffering processes. The contribution of injection and formation waters was observed in the $[Br^-]$ versus $[Cl^-]$ plot and the potential of scale formation is discussed through log correlation of $[Ba^{2+}]$ versus $[SO_4^{2-}]$. The overall method is fast and does not require the use of a time consuming reactor, making it a good one for a first evaluation of the aqueous phase composition during petroleum exploration and production.

1. Introduction

The aqueous phase present in petroleum is incorporated into the oil bulk as a water-in-oil (w/o) emulsion commonly named produced water, that can be originated from formation waters (connate or aquifer), or is a mixture of these with injection water (seawater). The latter is injected in the well during petroleum production and can have modified chemical composition whereas connate water is the interstitial fossil water that has followed petroleum formation and migration [1]. Formation waters are mostly Na-Cl brines, under-saturated with respect to sulfates and carbonates [2,3]. Works have reported that the concentration of total dissolved solids (TDS) in such brines are superior to 200,000 mg kg^{-1} and the concentration of alkaline and earth alkaline cations are correlated to chloride [4,5]. Within this consideration, important geochemical data, such as the origin of salinity and source apportionment of the aqueous phase, have been estimated by the determination of Li^+, Cl^- and Br^- concentrations together with isotopic ratios, such as $\delta^{37}Cl$ and $\delta^{81}Br$ [6,7].

It is of strategical importance for the industry to know the composition of the aqueous phase emulsified in petroleum. The volume and the salinity of this phase are used to estimate important reservoir parameters, such as the water saturation and resistivity, which are related to the quantity of petroleum within the reservoir, through Archie's Law [8–10]. As well, petroleum extraction yields water as a byproduct, and several issues are related to its composition, concerning concentrated and/or radioactive ions in the produced water, which represent a risk of environmental contamination for sediments and sea [11,12]. Additionally, the re-injection of produced water, diluted or modified, has been used alternatively to seawater in secondary or tertiary recovery of petroleum, lowering the formation of scale by precipitation of sulfates [13]. Even then, it is important to monitor the concentrations of ions, not only in the produced water but also in situ

throughout the flow paths, in order to build accurate models for the prediction of sulfates and carbonates scales formation and for the monitoring of scale inhibitors [14,15]. Analysis of cations and anions in produced water samples is usually performed by inductively coupled plasma optical emission spectrometry (ICP OES) and ion chromatography (IC), respectively, due to multielemental capability (ICP OES) and robustness [16,17].

Usually, the formation water composition is estimated by sampling and analyzing the water from the aquifer in the bottom of the oil-water zone, or by extracting and analyzing the water from cores obtained near this zone. However, both methodologies can be inaccurate, due to inhomogeneity within the zone [18]. In most cases, when petroleum is sampled near the oil-water zone, the aqueous phase forms a w/o emulsion with the oil phase that is difficult to separate, due to its stabilization by acidic ionized compounds and molecules present in the asphaltenes fraction, which is the heaviest and more polar fraction in crude oils [19–21].

In order to have phase separation, the use of a reactor unit with pressure and temperature control is generally time-consuming and needs to be executed in a properly equipped laboratory. Dilution with a known amount of water helps the separation of the aqueous phase [22], but is of limited application in the case of matrices with high percent of asphaltenes. By the contrary, the salinity of the water phase has a direct effect on surface tension at the w/o interface and some authors have shown that concentrations higher than 4000 mg kg^{-1} of TDS accelerate the coalescence of the water droplets [23]. Generally, demulsifiers are preferred to simple dilution for this process. These are hydrophilic compounds with high molecular weight, which solubilize in both water and oil phases, lowering the interfacial tension and allowing coalescence. The choice of the demulsifier and its optimal concentration depends on the concentration of the asphaltenes fraction [24,25].

In this work, a methodology was developed for the extraction of the aqueous phase directly from crude oil and the determination of its major cations and anions. The extraction method is based on the addition of known quantities of water and demulsifier to the crude oil sample and its recovery, after phase separation, for subsequent analysis. Major cations and anions concentrations were determined by ICP OES and IC, respectively. The extraction efficiency was evaluated by the mass balance of these elements between the crude oil samples and their aqueous extracts, whereas accuracy was evaluated by interlaboratory comparison results with the Petrobras Laboratory of Fluids, which uses phase separation with a reactor unit. The overall methodology was applied to crude oil samples and results were used to evaluate the origin of the emulsified waters and the potential for scale formation, showing its applicability for direct evaluation of petroleum salinity.

2. Experimental

2.1. Extraction of the emulsified water from crude oil samples

2.1.1. Samples, reagents and homogenization procedure

Samples of Brazilian crude oils were obtained from Cenpes (Centro de Pesquisas Leopoldo Américo Miguez de Mello), Petrobras. They originated from different Basins (A, B, C, D and E) and from different wells, identified by the number following the letter (for example, A1, A2, etc.). Differences in samples location within the well, or dates of production, are identified by a letter after the number (for example, B3a, B3b, etc.). Viscosity (Table 1), density and °API data were obtained from Cenpes, Petrobras and were in the range of 0.89 g mL^{-1} (A1) to 0.97 g mL^{-1} (E1) for density and 18 (C9) to 24.5 (D1d) for °API. The crude oil sample C2a was used for the development of the methodology. The pH was determined in some extracts and was around 4.

All solvents employed were of analytical grade. Ultra pure water was used throughout the experiments (18.3 MΩ cm, Milli-Q system, Millipore, Bedford, USA). Nitric acid (65.8% v/v, p.a., Vetec, Brazil) was purified by double sub-boiling distillation in a quartz apparatus

(Büchi, Switzerland).

Homogenization of the sample container was performed on a stirring plate for 30–45 min, then with an anchor type mechanical mixer equipped with a 13.2 cm Teflon coated propeller (Fisatom – model 713D, São Paulo, Brazil), at low speed (500 rpm) during 4 h. Aliquots of 20–50 mL were collected in the middle of the container and transferred to polyethylene flasks. The water amount in the aliquots was determined by Karl Fisher titration with an automatic titrator (model KF-1000, Analyser, São Paulo, Brazil) by potentiometric detection using a Pt electrode, calibrated with 25 μL of water. A mass of 0.2 g of the aliquot was diluted with a mixture of chloroform:methanol (3:1, v:v) and titrated with undiluted Karl Fischer solution (5 mg H$_2$O/mL of the titrant, Merck, Germany), according to the ASTM D 4377- (Standard Test Method for Water in Crude Oils by Potentiometric Karl-Fischer Titration).

2.1.2. Water – oil separation

The homogenization procedure generated water-in-oil (w/o) emulsions, which were kinetically stable for at least 48 h. Thus, emulsion breaking was necessary before extracting the water phase and was achieved with the addition of a demulsifier.

In the present work, the demulsifier was chosen according to its capability of breaking the w/o emulsion of crude oil C2a, of intermediate composition (Table 1, density: 0.93 g mL^{-1}, °API: 21.7). After homogenization, its water content determined by Karl Fisher was 4.65 ± 0.15%. The demulsifier was an alkoxylated alkyl phenol formaldehyde resin (Dow Química/Comab, Brazil), customized for Petrobras. The water phase was separated by the following procedure: duplicate of 20 g of homogenized crude oil and a similar mass of water were weighed at 0.1 mg in 50 mL high density polyethylene (HDPE) flasks and heated to 60 °C for 30 min in a thermostated bath, keeping this temperature throughout the procedure. Exactly 2 μL of the demulsifier were added and the solutions were mixed for 15 min at 700 rpm with the help of a propeller, adapted from disposable pipet tips (Brandtech™ Plastibrand™ PD-Tip™, Fischer Scientific, PA, USA), fixed in each flask cap. Then, the solutions were left standing for 1 h at 60 °C and the stirring and standing steps were repeated 3 times. The separation of phases was observed after centrifugation for 10 min at 2000 rpm (Centra MP4R Thermo IEC, USA). The aqueous phase was collected by means of a syringe with a chemically inert Teflon tube, then the aliquot of crude oil was extracted again, but at this time it was not necessary to add more demulsifier. The general scheme of the procedure, the propeller and the syringe used are shown in Fig. 1.

The two extracts were gathered and filtered on a polyvinylidene fluoride (PVDF) membrane (0.45 μm, Millipore, USA) in order to retain undissolved solids, if present. One aliquot was separated for the determination of anions by IC and another was separated and acidified with 0.1% (w/v) nitric acid in order to preserve the extracted solutions for the determination of cations by ICP OES.

2.2. Instrumental

2.2.1. Cations determination by ICP OES

The determination of Li, Na, K, Mg, Ca, Ni, V, Sr and Ba was performed with an inductively coupled plasma optical emission spectrometer Optima 4300DV (PerkinElmer, USA), equipped with a Meinhard concentric nebulizer and a cyclonic spray chamber (Glass Expansion, USA). High purity argon (99.996%, White Martins, Brazil) was employed and compressed air was introduced as shear gas. Multielemental Standard IV and monoelemental Standard Titrisol of Na, Ca, K, Mg (both: Merck, Darmstadt, Germany) were employed for the preparation of the analytical solutions, in 0.1% nitric acid, by weighing. The external calibration curves ranged from 0.01 to 0.5 mg kg^{-1}, or, when sample solutions were hypersaline: 0.5–100 mg kg^{-1}. Non-spectral interferences, such as by different salinities, were corrected by internal standardization with a monoelemental solution of Y (1000 mg kg^{-1}),