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Note

Compositional changes of diamondoid distributions caused by simulated evaporative fractionation

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ABSTRACT

We simulate and observe the effects of vertical migration on diamondoid composition for a single-phase fluid. A SGS Mini-PVT™ phase behavior cell was used to simulate upward migration of a condensate through multi-stacked reservoirs. PVT cell pressure was reduced from 4000 psi to 1000 psi in 1000 psi increments. At each pressure reduction step, the liquid phase of the condensate dropped out and samples were collected of both the liquid and gas phases. The liquid hydrocarbons were analyzed using GC and GC–MS to evaluate phase fractionation effects. The absolute and relative concentrations of diamondoids indicate that measurable compositional changes accompany simulated vertical migration.

1. Introduction

A commonly accepted model for the filling of conventional petroleum reservoirs states that petroleum is generated as supercritical phase and expelled from thermally mature source rocks at depth. Then, a single-phase mix of gas and liquids migrate upward through faults and permeable zones to gradually fill stacked reservoirs. Following initial expulsion from a source rock, pressure and temperature may be high enough to maintain a single-phase system, i.e. petroleum that is normally liquid at surface conditions remains in a gas phase. As expelled petroleum migrates to shallower depths, pressure and temperature generally decrease. With decreasing temperature and pressure, certain hydrocarbons become increasingly less soluble and drop out a liquid phase when they reach their respective dew points. The remaining single-phase mix of liquids and gases continues to migrate upward, repeating this process of phase separation multiple times while filling stacked-reservoirs. Over time, this process results in the removal of less soluble compounds from a migrating condensate and the enrichment of less soluble components in the early residual fractions.

Experimental data and observations made in various oil basins have identified petroleum that is greatly affected by migration fractionation. In particular, the composition of the C_5-C_8 gasoline range hydrocarbons and C_{15}+ alkanes can be altered greatly during migration related fractionation. Laboratory experiments by Chakhmakhchev et al. (1974), Chakhmakhchev (1983), Zhuze and Ushakova (1981), Price et al. (1983), Thompson (1987), England et al. (1991), Larter and Mills (1991), Carpentier et al. (1996), van Graas et al. (2000) have demonstrated measurable compositional changes for these hydrocarbons related to phase transformations at changing pressures and temperatures. It should be noted that the fractionation effect diminishes greatly as solubilities of hydrocarbons approach one another. Utilization of hydrocarbon ratios can further mask the indications of fractionation processes. Thus the works of Larter and Mills (1991) and van Graas et al. (2000) showed that biomarker isomer ratios, maturity indicators based on phenanthrenes, and C_1-C_4 carbon isotope ratios are relatively unaffected by migration fractionation.

The question posed in this study is whether diamondoid compounds are sensitive to migration fractionation or they are resistant to or even unaffected by such processes. It has been suggested that diamondoids are formed by the catalytic rearrangement of polycyclic hydrocarbons in subsurface environments (Petrov et al., 1974). In a more recent study, free-radical cracking reactions were proposed to explain the formation of the higher diamondoids (Dahl et al., 2010). Because diamondoids have extreme resistance to thermal stress, their absolute concentrations have been used to understand the extent of thermal cracking in highly mature oils (Dahl et al., 1999). Ratios of diamondoid isomers have also been used for maturity assessments in petroleum (Chen et al., 1996; Zhang et al., 2005; Fang et al., 2012). The resistance of most diamondoids, with the exception of adamantane, to secondary

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alteration processes has also made them useful as indicators of biodegradation in petroleum (Grice et al., 2000; Wei et al., 2007). Chakhmakhchev et al. (2016) suggested that factors other than thermal stress and cracking contribute to enriched diamondoid concentrations in petroleum. In this study, the vertical migration of a diamondoid-rich condensate was simulated to test whether diamondoid distributions are affected by migration fractionation.

2. Experimental

In this study, vertical migration of a gas condensate through stacked reservoirs was simulated to test whether diamondoid compositions are altered by phase fractionation. The condensate sample produced from the Eagle Ford formation in Texas was stored in a large glass container, which was properly sealed. The GC run of the pre-experiment sample showed minimal or negligible evaporation losses in the area of C_4-C_5. A condensate was combined with a gas mixture made up of 78% C_1 and 22% C_2-C_5. The condensate and hydrocarbon gas mixture was recombined in the SGS Mini-PVT™ phase behavior cell with floating piston and mixed to obtain a single-phase fluid at 5000 psi. Cell pressure was then reduced to 4000 psi and the sample was once again allowed to reach equilibrium between the liquid and the gas phases. All liquids that dropped out under the lowered pressure conditions were removed from the cell by flashing through a cold separator trap. A sample of the equilibrium gas phase at 4000 psi was also collected using the same method and conditions. The reduction in pressure was repeated for 3000, 2000, and 1000 psi. Samples of liquid hydrocarbons from the equilibrium gas and liquid phases were collected after each stepwise reduction in pressure (Fig. 1).

The n-alkane distribution in the liquid hydrocarbon samples collected from the equilibrium gas and liquid phases was measured using whole oil GC-FID. Whole oil samples were spiked with n-hexadecane-d34 internal standard prior to GC-FID analysis. Samples were analyzed using a high-resolution Agilent 6890 series GC system equipped with a Flame Ionization Detector (FID). Inlet temperature was set to 250 °C. A J&W DB-1 column (60 m × 0.32 mm × 1 μm) was used with helium as a carrier gas set to a flow rate of 2 mL/min. Samples were analyzed in split mode using a split ratio of eight. The initial oven temperature was held at 35 °C for 10 min. Oven temperature was then increased at a rate of 4 °C/min to 300 °C and held isothermal for another 76.25 min.

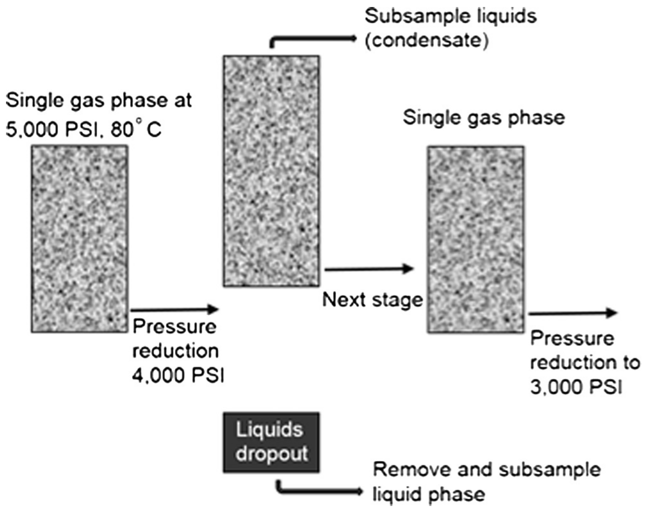

Fig. 1. Phase fractionation during simulated vertical migration using a PVT cell.

Absolute diamondoid concentrations were measured for the same samples using whole-condensate injection in GC–MS. Samples were analyzed using an Agilent 7890 series GC system coupled with a 7000 series MS. Inlet temperature was set to 300 °C. Samples were analyzed in splitless mode. A J&W DB-5 column (60 m × 0.25 mm × 0.25 μm) column was used with helium as a carrier gas set to a flow rate of 1.34 mL/min. The initial oven temperature was held at 40 °C for 1.5 min. Oven temperature was then increased at a rate of 4 °C/min to 310 °C and held isothermal for another 33.5 min. Selective Ion Monitoring (SIM) was used to collect data for selected diamondoids using m/z = 135, 136, 163, 187 and 201 ions. The individual diamondoids were identified using elution patterns published in literature. Both integrations in GC and GCMS runs were done based on peak areas. No compound class fractionation was been done prior to GC and GCMS analyses. Absolute concentrations were calculated using internal standards of n-dodecane-d26 for the diamondoid compounds.

3. Results

The phase fractionation effect on n-alkane distribution has been documented in studies by Thompson (1987), Curiale and Bromley (1996) and van Graas et al. (2000). A ratio of short to long chain alkanes ($C_{15}/(C_{15} + C_{25})$) was used to quantify compositional changes in the condensate samples. The decrease in abundance of C_{13}+ alkanes in our experimental fluid recovered from the gas phase at 1000 psi relative to the original condensate indicates the successful simulation of the phase fractionation effect (Fig. 2).

The observed sensitivity of diamondoid compounds to phase fractionation varied. Absolute concentrations of diamondoids measured using GC–MS indicated that fractionation had the greatest effect on lighter adamantanes. On average, absolute concentrations for the adamantanes were enriched by 23% in the final condensate (Table 1).

The greatest enrichment of diamondoid compounds in the final condensate was seen for adamantane, 1-methyladamantane, 1,3-dimethyladamantanes, and 1.3.5-trimethyladamantane. The concentrations of these four diamondoids were generally greater in the gas phase samples relative to the liquid phase samples for the same pressure. However, some other adamantanes decreased during the phase fractionation simulation. The 1-and 2-ethyladamantanes preferentially accumulated in the liquid phase during phase fractionation and their concentration dropped significantly in course of the experiment. At this point, we do not have a full understanding of the mechanism resulting in the fractionation of adamantane compounds. The differences of solubility in gas under the experimental P and T conditions applied could result in the preferential accumulation of various compounds either in gas or liquid phases and their relative enrichment/depletion in modeled condensates during simulation.

Not all of the lighter adamantanes demonstrated definitive trends toward either enrichment or depletion with phase fractionation. The absolute concentrations for 2-methyladamantane, 1,2-dimethyladamantane, and the tri- and tetra-methyladamantanes were enriched after the first three fractionations but were greatly reduced in the final pressure step of 1000 psi. This reversal of abundance may be related to the small volume of liquid recovered from the PVT cell during the final pressure step at 1000 psi causing elevated method error.

Unlike the lighter adamantanes, the absolute concentrations for the later-eluting, higher molecular weight diamondoids consistently decreased (up to 86%) with phase fractionation. The absolute concentrations of the later-eluting diamondoids were always higher in the liquid phase than in the corresponding gas phase sample at every pressure step, which suggests their lower