Partitioning of metal ions between water and petroleum at geological temperatures: an experimental study

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PARTITIONING OF METAL IONS BETWEEN WATER AND PETROLEUM AT GEOLOGICAL TEMPERATURES: AN EXPERIMENTAL STUDY

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In the context of energy transition, the quest of metal resources has become of strategic importance. A specific focus is currently being placed on basinal brines as alternative source for metals as exemplified by the search for lithium in the Rhine Graben (France), a chemical element of prime importance for battery manufacturing. This perspective brings potential opportunity to value saline waters present in oil fields. The solute content of basinal waters is a consequence of water-rock equilibrium reactions. Anomalous enrichment of brines in metals is therefore primarily linked to mineralogical peculiarities of rock formations and/or to specific dissolution/complexation mechanisms. While aqueous chemistry and thermodynamic databases are available as to explain observed water chemical compositions, very few literature includes the influence of petroleum. However, literature on ore deposits describes bitumen or petroleum strongly enriched in metals. In some cases, these enrichments are explained in terms of complexation or redox reactions. Yet, anomalous enrichment mechanisms are often not clearly understood. Dissolution of metals by petroleum are also described and the possibility for petroleum to be a metal carrier implied in ore deposit formations is often evoked but not well constrained. A possible reason for confusion concerning the role or influence of the presence of petroleum on metal capture, transport, deposition in the literature is that a comprehensive experimental and theoretical background capable of describing the water-rock-petroleum system is still very incomplete. This may have consequences on our understanding of metal composition in oil and accompanying waters in petroleum fields.

In order to investigate this issue we conducted a series of experiments exploring the partitioning of metal ions between water and petroleum at temperatures up to 150°C.

<u>Aqueous solution-oil contact experiments.</u>
Aqueous solutions of metal salts representative of basinal brines were prepared by considering literature data on chemical composition of both sedimentary formation waters and paleofluids trapped as fluid inclusions. To simulate the interactions between oil and formation water, contact experiments between oil samples and aqueous solutions with different metal ions as chlorides ($Cu^{2+,}$ Li^{+}, Co^{+}, Ag^{2+}, Ni^{+}) were performed. Nine grams of aqueous solution (e.g. 1 mol/L of NaCl and 7.44×10^{-4} mol/L of $CuCl_2$**)** and one gram of oil were loaded in gold plated stainless steel reactors. The reactors were closed under argon atmosphere with a gold lined stainless steel cap. For heating, the reactors were placed in an oven at 150°C for duration of 6 hours to 1 month. At the end of the contact experiment, the reactors were removed from the oven and quenched in cold water. After opening the reactor, reacted oil and water phases were separated by pipetting the water phase and the oil was recovered using dichloromethane (DCM) to facilitate the separation and minimize the loss of material. The DCM was evaporated using rotary evaporator and a stream of nitrogen. Oil was inserted in silica capillaries and then analyzed by laser ablation ICP-MS to determine metals contents.

The experimental results at 150°C show that metal concentrations in oil increases with time as to reach a maximum value after a minimum of 10 days. For copper for instance concentration in oil reaches a maximum of 20ppm.

^{1}H-NMR experiments.

In order to better understand the possible mechanisms of metal transfer from aqueous solution to oil, water-oil contact experiments were conducted at temperatures between 40 and 200°C within an NMR spectrometer. The objective was to test if water was present in oil phase during heating. A closed capillary filled with DMSO-D_6 (as a reference for the chemical shift) was loaded together with oil and water in 1/1 volume ratio into 3mm ID NMR tubes sealed at both ends. The heating was conducted on a 300 MHz NMR spectrometer equipped with a specific high temperature probe from 40 to 200°C at 20°C and 40°C steps. Spectra were recorded for solely the oil phase at each temperature. The shape and the chemical shift of peaks were followed. Two peaks could be attributed to water in oil (Figure 1). A peak at about 4.7ppm is interpreted as water droplets phase. A peak at about 3.6ppm is at a position similar to what is observed for water in solution in acetonitrile (a fully miscible solution). With increasing temperature, both peaks show a displacement to lower chemical shift values following a linear trend, yet with different slopes. This indicates two distinct relationships between water molecules and their surrounding solvation environment.

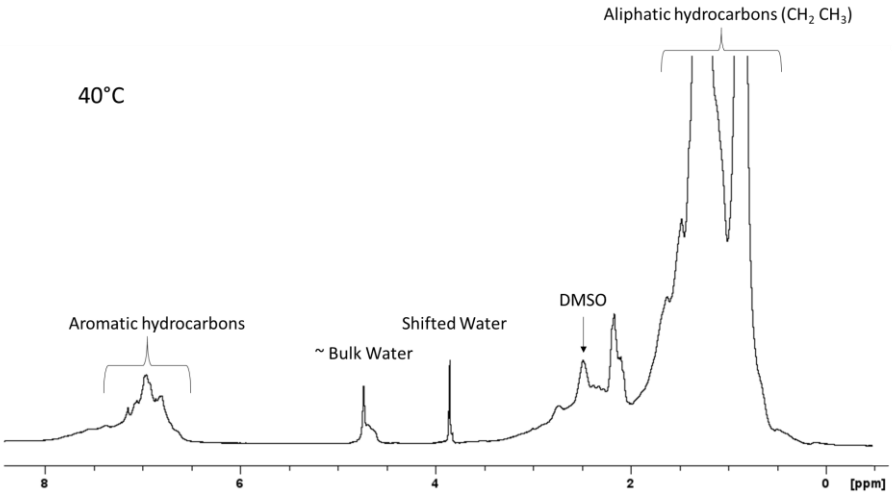

Figure 1: ^{1}H-NMR spectrum of oil obtained for an oil/water in 1/1 volume ratio system at 40°C. Two distinct peaks attributed to water are observed.

Conclusion. Systematic experimentation at geological temperatures allows to documents the partitioning of different metal species between water and oil. Such data is not commonly found in literature. The use of NMR brings background to the transfer mechanisms of metals between water and oil, considered as co-existing solvents. The existence of water under different states (from droplets to totally dissolved) in the NMR spectra may be indicative of water dissolution into oil as a possible initiation step for metal transfer.

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