ELSEVIER

Journal of Geochemical Exploration 69–70 (2000) 663–668

JOURNAL OF GEOCHEMICAL EXPLORATION

www.elsevier.nl/locate/jgeoexp

Water in petroleum inclusions: evidence from Raman and FT-IR measurements, *PVT* consequences

J. Pironon[a,*], R. Thiéry[b], S. Teinturier[a], F. Walgenwitz[c]

[a]*UMR G2R 7566—(CREGU, CNRS, Université Henri Poincaré, INPL) BP239, F-54506 Vandúuvre-lés-Nancy Cedex, France*
[b]*Université B. Pascal, Département des Sciences de la Terre, 2-5 rue Kessler, 63038 Clermont-Ferrand, France*
[c]*ELF, CSTJF, Avenue Larribau, 64018 Pau Cédex, France*

Abstract

Petroleum inclusions cannot be considered as water-free inclusions. New Raman and FT-IR experiments have shown solubility of water in hydrocarbons trapped in inclusions for temperature conditions of natural petroleum reservoirs. Water dissolved in a hydrocarbon phase appears at 3630 cm^{-1} on the Raman spectrum and its Raman fingerprint is totally different from the Raman signature of liquid water in the 3250–3450 cm^{-1} range. Raman microscope has been coupled with a heating stage to follow water solubility with temperature increase. However, Raman analyses cannot be applied to petroleum inclusions: their fluorescence masks the Raman signal. Similar experiments have been made using FT-IR microspectroscopy on synthetic and natural inclusions. Intensity of the liquid water infrared band decreases with temperature increase due to solubility of water in the oil phase. Therefore, bulk homogenisation temperature of a petroleum inclusion is obtained when the liquid water band, centred at 3400 cm^{-1}, disappears from the FT-IR spectrum. When aqueous inclusions are associated with petroleum inclusions, homogenisation temperatures of the two inclusion types should be similar. *PVTX* interpretations of petroleum inclusions should therefore be reconsidered.

Keywords: petroleum inclusions; Raman microspectroscopy; FT-IR microspectroscopy; water solubility in hydrocarbons; homogenisation temperature

1. Introduction

Hydrocarbon in petroleum environments can be trapped in aqueous inclusions or in petroleum inclusions. Aqueous inclusions are frequently enriched in methane gas, which can be quantified by Raman microspectroscopy (Dubessy et al., 2000). Other hydrocarbons (ethane, propane) or gases (CO_2, N_2, H_2S) should be present in inclusions but have concentrations below the detection limit of the Raman method. Petroleum inclusions in salt or fluorite are often filled with an oil–water immiscible mixture. The water phase is rarely observed in petroleum inclusions from sandstones in deep oil reservoirs. It is supposed to be present as a non-visible liquid film, wetting the inclusion walls. *PVTX* interpretations of oil migration consider neat hydrocarbon inclusions and do not take into account the presence of water.

Data from the literature show that water is always soluble in hydrocarbon whatever the nature of the hydrocarbon (Fig. 1). The concentration of water in hydrocarbon phases exponentially increases with temperature and reaches about 1% at 150°C.

The objective of this paper is to show (1) the ubiquitous presence of water in petroleum inclusions and its solubility at high temperature and (2) the

* Corresponding author. Tel.: + 33-383-9138-20; fax: + 33-383-9138-01.

E-mail address: jacques.pironon@g2r.u-nancy.fr (J. Pironon).

0375-6742/00/$ - see front matter
PII: S0375-6742(00)00108-4

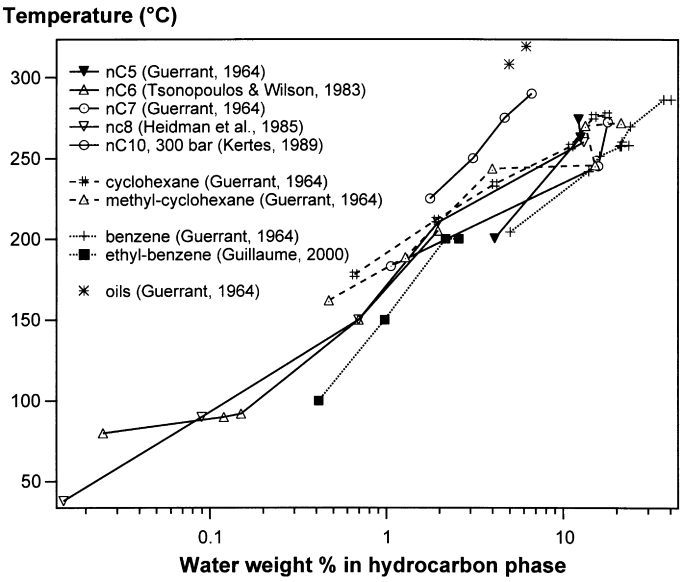

Fig. 1. Weight percent of water in hydrocarbon phase vs. temperature for five *n*-alkanes, two cycloalkanes, two aromatics and one oil. (See Guerrant, 1964; Guillaume et al., 2000; Heidman et al., 1985; Kertes, 1989; Tsonopoulos and Wilson, 1983.)

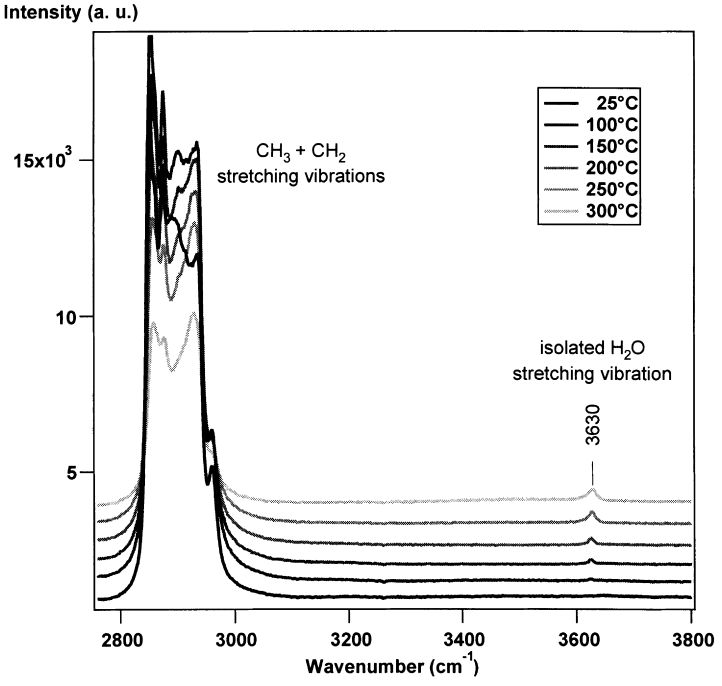

Fig. 2. Raman spectra at different temperatures of an *n*-dodecane inclusion synthesised in KCl.

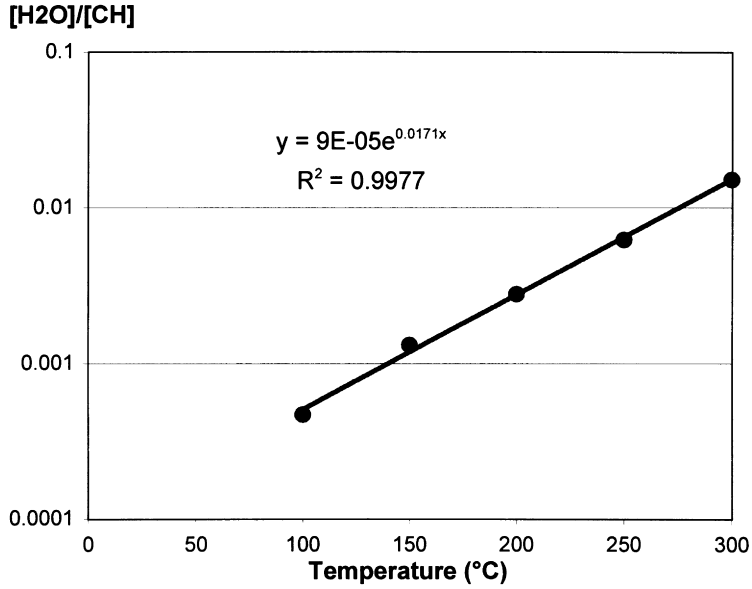

Fig. 3. Evolution of the H_2O/CH band area ratio measured on Raman spectra with temperature for an *n*-dodecane synthetic inclusion in KCl.

consequences on pressure–temperature reconstruction and understanding of oil migration phenomenon.

2. Methods and material studied

Natural petroleum inclusions from MVT deposit (Illinois, USA) and synthetic oil inclusions were used. Natural samples have two main advantages: (1) inclusions are trapped in fluorite that is transparent in mid-infrared range; and (2) inclusions with variable water/oil volumetric ratios (from water dominant to oil dominant) are associated on the same planes. Synthetic inclusions were created in KCl crystals following Pironon's method (Pironon, 1990), from *n*-dodecane and natural degassed oil.

Raman spectra were acquired with a Labram© Dilor microspectrometer linked to an Argon laser with an incident radiation of 514.5 nm. Microspectrometer was coupled with a Chaixmeca microthermometric stage to follow the evolution of the Raman spectra with temperature. FT-IR spectra were recorded at LEM laboratory (Nancy, France) with an IFS 55 Bruker spectrometer linked to an infrared microscope coupled with a Linkam heating stage.

OH and CH molecular groups from water and oil, respectively, are detected in Raman and FT-IR spectra by their characteristic stretching and bending vibration areas. For this study, stretching bands were considered and their integrated intensities (i.e. band areas) were measured.

3. Results and analyses

Evidence of water in hydrocarbon inclusions was shown using Raman backscattering on synthetic non-fluorescent inclusions. Spectra were recorded focusing the laser beam inside the hydrocarbon phase of a three-phase inclusion (liquid water, liquid hydrocarbon, and vapour). Contribution of surrounding water phase was rejected, decreasing the confocal hole of the Labram microspectrometer.

Spectra recorded between 25 and 300°C at saturated vapour pressure are plotted in Fig. 2. Presence of dissolved water is clearly observed for the first time at 3630 cm^{-1}. This water contribution was totally different from the liquid water Raman band, which was bimodal with two maximums at 3250 and 3450 cm^{-1}. This band location was coherent with isolated water molecules like water vapour. No hydrogen bonding was detected. The $[H_2O]$/[CH] band area

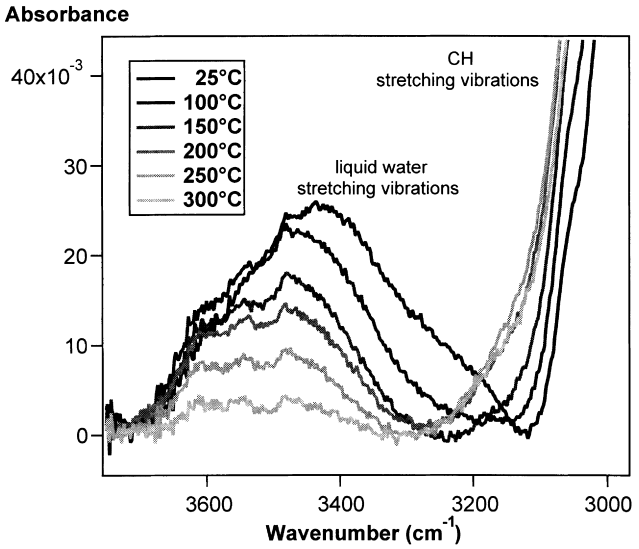

Fig. 4. Evolution of the FT-IR spectra with temperature of a synthetic petroleum dominant inclusion in KCl. Intensity of liquid water stretching bands decreases with temperature increase.

ratio increases with temperature (Fig. 3) with similar exponential evolution as in Fig. 1.

Raman analysis of hydrocarbon cannot be applied to natural petroleum inclusions because of fluorescence. Emission of fluorescence is induced by laser excitation of aromatic molecules and masks the Raman signal.

In the case of natural inclusions, FT-IR spectroscopy is more efficient than Raman spectroscopy because it is not affected by fluorescence. It can also detect the presence of water in petroleum inclusions but has lower spatial resolution; minimum analytical spot size is 10 μm instead of 1 μm for Raman. The IR beam is reduced to the size of the bulk inclusion. Liquid water stretching vibrations are located at 3200 and 3400 cm^{-1}. They are clearly

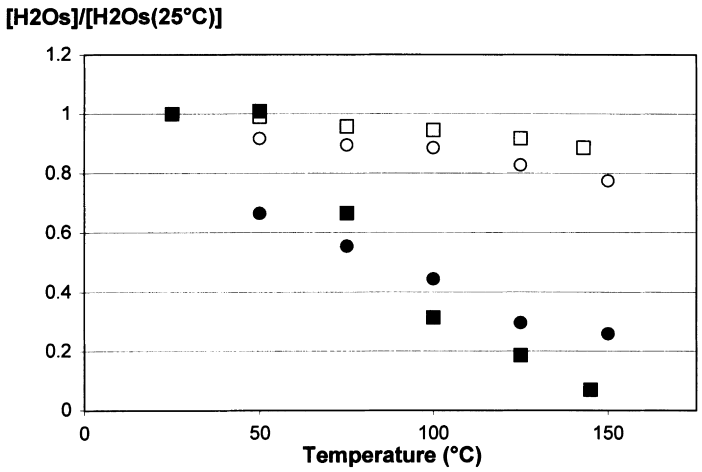

Fig. 5. Evolution with temperature of the FT-IR band area ratio between liquid water at experiment temperature and liquid water at 25°C for natural inclusions in fluorite from Illinois (USA). Open squares: aqueous inclusion; open circles: aqueous inclusion with oil droplet; filled circles: oil inclusion with visible liquid water meniscus; filled squares: oil inclusion without visible water.

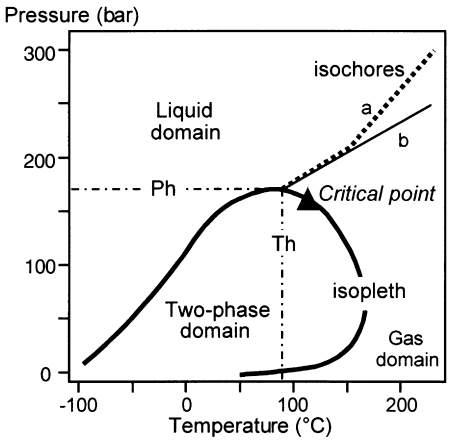

Fig. 6. P–T diagram for a model oil inclusion with a homogenisation temperature (T_h) of 90°C and a homogenisation pressure (P_h) of 170 bar. (a) Isochore for oil + 10 mol% of water, (b) isochore for pure oil system.

detected on the spectrum of a synthetic oil inclusion at room temperature. Their intensity decreases with temperature (Fig. 4). The volume of the liquid water phase within the inclusion decreases. This phenomenon is related to the increase of water solubility in oil.

The liquid water band area was measured at 25°C and at different temperatures for different natural inclusion types from MVT fluorite deposit (Illinois): aqueous inclusion, aqueous inclusion with oil droplet, oil inclusion with visible liquid water meniscus and oil inclusion without visible water. The FT-IR band area of liquid water [H_2O] at a given temperature was normalised to the liquid water band at 25°C [H_2O(25°C)]. The [H_2O]/[H_2O(25°C)] ratio was equal to 1 at 25°C and 0 at the bulk homogenisation temperature of the inclusion. Aqueous inclusions from Illinois show a slight decrease of the liquid water band area with temperature, which can be explained by a decrease of the infrared absorption with temperature (Fig. 5). When hydrocarbons are present in the water phase (fluid inclusion with oil and water immiscible phases) a more important decrease of the liquid water band area is observed: a water fraction has been dissolved in oil. For oil dominant inclusions, the decrease of the liquid water band area is important and the slope of the trend increases when the water content decreases. Inclusion with no visible water phase was probably trapped in a homogeneous state. Its normalised liquid water band area gives the bulk homogenisation temperature (150°C) when it becomes equal to zero. This temperature is higher than the homogenisation of the oil phase (120°C) and is similar to the homogenisation temperature of the aqueous inclusions (143°C).

4. Discussion and conclusions

Coupled with a heating stage, FT-IR analysis allows us to determine the bulk homogenisation (water in oil) temperature of petroleum inclusions. Bulk homogenisation is never measured by conventional microthermometric studies, which only take into account the homogenisation of the oil phase. These new data should help us to reconsider *PVTX* interpretations of petroleum inclusions.

The "water effect" on isochore has been tested using Daridon (1992) equation of state on a model inclusion with homogenisation temperature at 90°C. Two different ways of calculation were chosen taking (a) or not taking (b) into account the presence of 10 mol% of water (Fig. 6). At low temperature, between 90 and 150°C, the isochore is linear and is superimposed to the isochore of a pure oil system (b). At high temperatures (>150°C) the isochore shows a curvature and differs from the isochore of the pure oil system (b).

It appears from this simulation that the presence of water in hydrocarbon does not drastically modify *PT* properties of the inclusion. Therefore, when petroleum and contemporary aqueous inclusions are present, trapping pressure and temperature could be obtained by intersection between hydrocarbon and aqueous isochores.

Nevertheless, when petroleum inclusions are not associated with contemporary aqueous inclusions, bulk homogenisation should be measured by FT-IR spectroscopy and can be interpreted as trapping temperature and pressure. The bulk homogenisation temperature of an oil inclusion, containing liquid water, liquid and vapour oil, may be some tens of degrees higher than the homogenisation temperature of its oil phase.

References

Daridon, J.L., 1992. Mesure et représentation des équilibres de

phases sous pression de mélanges díeau, de paraffines et de dioxyde de carbone. Thesis, University of Pau, France, 177pp.

Dubessy, J., Buschaert, S., Lamb, W., Pironon, J., Thiéry, R., 2000. Methane-bearing aqueous fluid inclusions: Raman analysis, thermodynamic modelling and application to petroleum basins. Chem. Geol. (in press).

Guerrant, R.P., 1964. Hydrocarbon–water solubilities at high temperatures under vapor–liquid–liquid equilibrium conditions. Ph.D. thesis, Pennsylvania State University, 124pp.

Guillaume, D., Tkachenko, S., Dubessy, J., Pironon, J., 2000. Submitted for publication.

Heidman, J.L., Tsonopoulos, C., Brady, C., Wilson, G.M., 1985. High-temperature mutual solubilities of hydrocarbons and water. Part II: ethylbenzene, ethylcyclohexane, and *n*-octane. AIChE J. 31, 376–384.

Kertes, A.S., 1989. Hydrocarbons with Water and Seawater. Part II: C8 to C36, vol. 38, Pergamon Press, New York.

Pironon, J., 1990. Synthesis of hydrocarbon fluid inclusion at low temperature. Am. Mineral. 75, 226–229.

Tsonopoulos, C., Wilson, G.M., 1983. High-temperature mutualsolubilities of hydrocarbons and water. Part I: benzene, cyclohexane and *n*-hexane. AIChE J. 61, 815–817.