EXPERIMENTAL STUDY OF PHASE TRANSFORMATION OF HYDROCARBONS IN WATER-OIL MIXES AT ELEVATED AND HIGH TEMPERATURES AND PRESSURES Balitsky V.S., Bondarenko G.V., Balitskaya L.V., Novikova M.A., Bublikova T.M. (IEM RAS), Penteley S.V. (Montpellier, France) balvlad@iem.ac.ru

Key words: Fluid inclusions, synthetic quartz, oil, methane, solid bitumen

The present study determines the hydrocarbons phase transformations which occur at interaction of natural petroleum with hydrothermal fluids. Experiments were carried out in autoclaves of 30 and 50 cm³ in volume at temperatures 180-500°C and pressures 1-150 MPa, accordingly. The content of petroleum in initial water mixes was from 0.01 to 50 vol. %. The experimental runs were carried out under conditions of direct temperature gradient that allowed both the water-hydrocarbons interaction and growth of quartz crystals which capture fluid inclusions. These inclusions were the basic data storage of phase transformations of hydrocarbons. They were studied by methods of thermobarometric geochemistry.

It was defined that water-hydrocarbon fluids can be found in various phase states in the field of elevated and high temperatures and pressures. These phase states depend on thermo-baric parameters and volumetric ratios of aqueous fluids (L1), petroleum (L2), hydrocarbon gases, basically methane (G1) and water vapour (G2). The water-hydrocarbon systems represent practically not soluble each in other stratified mixes of water solution and petroleum, and partially dissolved free hydrocarbon gases at ambient temperature and pressure. However, the situation changes at temperature and pressure rise. When petroleum and gas have approximately equal volumes and their sum concede a water solution in 2-3 or more times (V2 \approx V {G1+G2} and VL1>> VL2+V {G1+G2}, where V is the volume of a corresponding phase) the gas phase is completely dissolved in petroleum and water solution with formation of diphase water-petroleum fluid (L1+L2) at temperature rise to 300-330°C (fig. 1). The permanent existence of such gas-free fluid was observed experimentally up to temperatures 385-405°C. The estimated amount of dissolved liquid hydrocarbons (light and middle weight petroleum fractions) in aqueous phase of fluid reaches 6-8 vol. %. Thus, the general tendency in increasing of solubility of liquid hydrocarbons in water fluids does not exclude a possibility of the essentially higher values of dissolution of liquid hydrocarbons up to full miscibility with water at the higher thermo-baric parameters.



Fig.1. The water-hydrocarbon essentially liquid inclusions in synthetic quartz crystal with phase ratios: VL1 > VG + VL2 and $VG \ge VL2$, where V - volume of phase in inclusion, L1 - aqueous solution, L2 - liquid hydrocarbons, G - gas (mainly methane + water vapor.

At other phase ratios, the water-hydrocarbon fluids can exist at high temperatures and pressure as well heterogeneous as homogeneous states. It is experimentally shown that their transition from heterogeneous to homogeneous state is carried out as well to gas as to liquid phases. The homogeneous gas fluid arises at predominance of gas above petroleum and water solution in 3-4 or more times, and a

water solution above petroleum in 2-3 times (V {G1+G2}>> VL1+VL2 and VL1> VL2). At temperature rise, it was observed firstly a full dissolution of liquid hydrocarbons in gas (325-335°C) and only after that, in the temperature range of 350-360°C, a full homogenization of fluids with a gas phase begins (fig. 2). The excess of water solution in several times above gas, and gas - multiply above liquid hydrocarbons (VL1> V {G1+G2} and V {G1+G2}>> VL2) were resulted to the first dissolution of these hydrocarbons in gas at 250-280°C. Then, in the temperatures range of 365-380°C, this hydrocarbon phase is completely dissolved in a water solution with formation of a liquid homogeneous fluid (fig. 3). And, finally, in a case when petroleum predominate above gas and water solution in 2-3 times, and volumes of water and gas phases are approximately equal (VL2> VL1+V {G1+G2} and VL1≈V {G1+G2}), in the beginning, gas dissolution in liquid hydrocarbons are observed at 230-280°C, and then the water solution is completely dissolved at temperatures 350-360°C in the liquid hydrocarbon phase (fig. 4).









1.2

SB

LI

Fig.3. On the top: a water-hydrocarbon inclusion in synthetic quartz crystal with a phases ratio VL1 \geq (VG + VL2) and VG >>VL2 where V - volume of phase in inclusion, L1 - aqueous solution, L2 - liquid hydrocarbons, SB - solid bitumen, G - gas (mainly methane). Photographs below: fragment of microthermogram of an inclusion. Liquid hydrocarbons are completely dissolved in gas at T=257.4 °C. The full homogenization in a liquid phase occurs at T=367.5 °C (L - homogeneous fluid). Conditions of capture of the inclusion: aqueous solution of 3 wt/ % Na₂CO₃, T=490 °C, P=150 MPa



As a whole, the study confirms an essential role of the hydrothermal solutions in the processes of migration of liquid and gaseous hydrocarbons. The indicated thermo-baric parameters significantly exceed temperatures (on 100-200°C) and pressures (on 10-100 MPa) observed in current petroleum and gas basins. At the same time, the study of the behaviour and phase transformations of hydrocarbons in hydrothermal fluids at chosen thermo-baric parameters allows to perceive the conditions of presence and migration of hydrocarbons in the zones of deeper metamorphism caused by driving to depths or warming by magmatic rock bodies of gas-petroleum substances.

This work is supported by RBRF (Grant № 09-05-0074)

Electronic Scientific Information Journal "Vestnik Otdelenia nauk o Zemle RAN" № 1(27) 2009 ISSN 1819 – 6586 Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2009 URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2009/informbul-1_2009/hydroterm-4e.pdf

Published on July, 1, 2009 © Vestnik Otdelenia nauk o Zemle RAN, 1997-2009 All rights reserved