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GEOLOGY

Regularities in the Behavior of Hydrocarbon Systems of Oil and Gas Pools

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This paper considers the results of experimental investigations that confirm the important role of sorption in phase transformations in the productive collector and the distribution of hydrocarbon components between stationary and recoverable parts of the system. Sorption of high-boiling components of the bedded hydrocarbon mixture on walls of pore channels can change the composition of a filtering fluid. A decrease in the cross section of filtration channels can be accompanied by reduction of bed permeability and, as a consequence, hydrocarbon output. This is especially true of the methodology of laboratory experimentation.

Reduction of permeability due to adsorption during oil filtration in sandy collectors was reported in [1, 2] as far back as the 1940s. Formation of the adsorption bed in oil pools changes the molecular nature of the solid surface and produces a colloidal boundary layer of oil. Its viscosity is an order of magnitude higher compared to that of oil in the collector, and its thickness is commensurable in some cases with the radius of pore channels [3].

The authors of [4] demonstrated that the porous medium exerts a considerable influence on phase transformations, in particular, on the evaporation of retrograde condensate exuded in the bed during the injection of "dry" hydrocarbon gas into the bed model.

Phenomena determined by the molecular interaction of fluids with pore walls play a great role in the gas condensate or oil bed that represents a highly dispersed porous medium with a developed surface. The mechanism of these phenomena is, however, insufficiently understood to be taken into account quantitatively in the development of hydrocarbon pools. This is particularly true for hydrocarbon pools put into operation in the Achimovian and Lower Cretaceous rocks of West Siberia.

To describe the fluid phase behavior in the pore space, one should have data on the quantity of adsorbed hydrocarbon components depending on pressure at different temperatures. One can obtain such data using high-precision equipment that increases substantially the accuracy and reliability of results.

The experimental complex designed to study the phase behavior of hydrocarbon mixtures in dry and water-saturated porous media [5] consists of two adiabatic calorimeters constructed in accordance with the specificity of the problems to be solved. The first calorimeter is destined for studying fluids in a free volume, while the second calorimeter is meant for investigations in a porous medium. The investigations were carried out according to the certified method [6].

The phase behavior of hydrocarbon mixtures in porous media is investigated using fractionated sand (dry nonextracted powder of ground quartz with grain sizes 2.3 and 31.5 μm with a specific surface of $1.160 \cdot 10^6$ and $0.104 \cdot 10^6$ m^2/m^3, respectively). To study the influence of water on the phase behavior of hydrocarbon mixtures, sand is saturated with water up to the assigned saturation level. The experimental complex allows us to investigate within the temperature range of 90–425 K and pressure range of 0.1–75.0 MPa with an error of ±0.0005 K and ±0.0007 MPa, respectively.

The studies are carried out by two independent and supplementing methods.

(1) The first method is based on the measurement of the thermal parameters (pressure and temperature). The boundary curves of hydrocarbon mixtures are defined by the following fact: when heating a substance, the heat capacity shows an anomalous behavior (jump) at the temperature transition from one phase state into another (for instance, from the two-phase state into the single-phase state). Correspondingly, the pressure versus temperature dependence experiences a bend (also a jump in the derivative). Precisely these anomalies are used to determine the temperature and pressure on the

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boundary curve for a given density and concentration of the substance.

(2) The second method is based on measurement of the calorimetric parameters (heat of phase transitions and heat capacity). The quantity of the adsorbed component is determined on the basis of heat of hydrocarbon crystallization in sand and the free volume.

Figure 1 demonstrates phase diagrams of the hydrocarbon mixture of one and the same composition in the free volume and porous media represented by fractionated sand samples described above. The mixture composition (mol %) is given in the table (mixture 1). As is seen from the figure, the phase behavior of hydrocarbons in sand with a medium grain size of 31.5 μm distinctly differs from their phase behavior in the free volume. Quantitative transformation of the phase diagram occurs as the result of adsorption and desorption. Adsorption of 12–13% heptane at a pressure of 6.1 MPa provokes a shift of the boundary curve of the starting mixture toward reduced temperatures by 5–6 K.

Our previous experiments with individual components demonstrate that adsorption of methane and propane by fractionated sand is very low. However, further experiments showed that if these components are mixed with more high-boiling hydrocarbons (for instance, heptane), adsorption of the latter component enhances the sorption of methane and especially propane (dissolution and adsorption of these components in the sorbed heptane film). The boundary curve in sand at temperatures below 347.5 K passes above the corresponding boundary curve in the free volume because of the sorption of propane.

To check the fact of propane sorption, we investigated several three-component mixtures with heptane in the free volume. The concentration of propane and methane was varied. The experiment with mixtures of type 1 (table) containing additional heptane (2–4.5 mol %) showed that decrease in the content of propane (analog of its adsorption) promotes an increase in the phase transition pressure at the specified temperature.

The influence of fractionated sand on the phase behavior of the methane–propane–heptane mixture is more distinct in experiments with the input and recovery of the substance (Fig. 1). To eliminate the influence of phase transitions unrelated to sand, the substance is recovered under thermobaric conditions corresponding to a single-phase state of the mixture in the free volume. The input of the substance is started at the density corresponding to the phase transition at point *C*' and terminated at the density corresponding to the phase transition at point *A*'. The recovery of the substance is started at the density corresponding to the phase transition at point *A*' and terminated at the density corresponding to the phase transition in point *G*'. Since the recovered mixture is relatively enriched in methane and propane due to adsorption of high-boiling components, a decrease in pressure and an increase in temperature lead to desorption of the adsorbed heptane and the consequent growth of its concentration in the vapor phase.

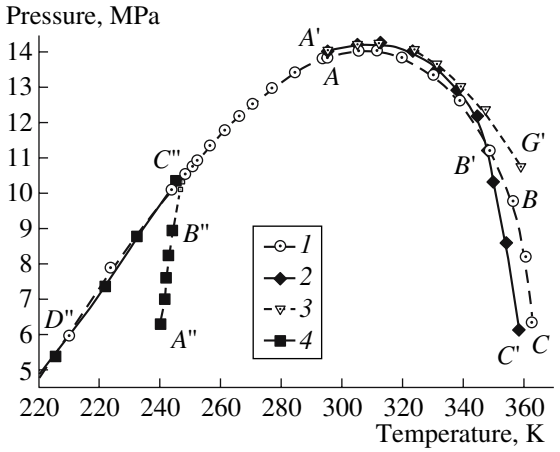

Fig. 1. Phase diagrams of three-component hydrocarbon mixture 1 in the free volume and fractionated sand. (*1*) Free volume; (*2*) sand, 31.5 μm, HC mixture input; (*3*) sand, 31.5 μm, HC mixture recovery; (*4*) sand, 2.3 μm, HC mixture input.

Investigations of the fractionated sand sample with an average grain size of 2.3 μm and a large specific surface (consequently, high sorption capacity) revealed considerable changes in the composition of the hydrocarbon mixture in the sand pore volume. Consequently, we recorded not only quantitative transformation of the fluid phase diagram compared to that in the free volume, but also the qualitative transformation. This is shown by the results presented in Fig. 1.

Qualitative transformation of the phase diagram in coarse-grained (31.5 μm) sand is manifested in variation of the boundary curve shape: branch *ABC* is transformed into *A*'*B*'*C*'. In fine-grained (2.3 μm) sand, both heptane and propane are adsorbed considerably due to the great specific surface, resulting in the formation of two boundary curves.

The first branch *A*"*B*" corresponds to the relatively low density of the mixture (less than 230 kg/m^3). In this case, the adsorption capacity of the fine-porous medium is sufficient to sorb all the heptane and part of the propane, resulting in a phase transition in the binary (methane–propane) mixture.

Composition of hydrocarbon mixtures

Component	Mixture no.			
	1	2	3	4
CH_4	79.8	76.0	77.4	78.2
C_3H_8	17.2	19.2	19.6	19.8
C_7H_{16}	3.0	–	–	–
$C_{16}H_{34}$	–	4.8	3.0	2.0

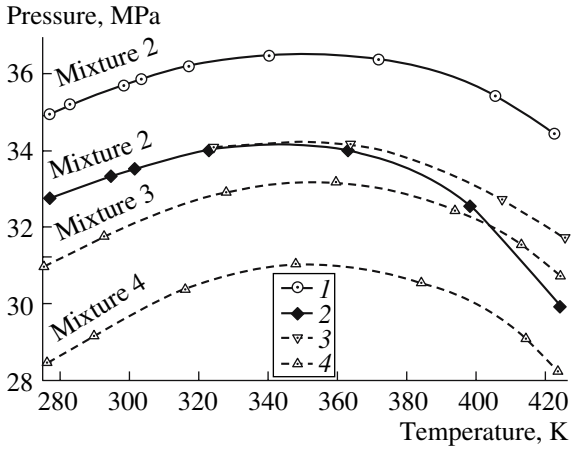

Fig. 2. Phase diagrams of three-component hydrocarbon mixtures 2, 3, and 4 in the free volume and fractionated sand. (*1*) Free volume, mixture 2; (*2*) sand, 31.5 μm, mixture 2, HC mixture input; (*3*) sand, 31.5 μm, mixture 2, HC mixture recovery; (*4*) free volume, mixtures 3 and 4.

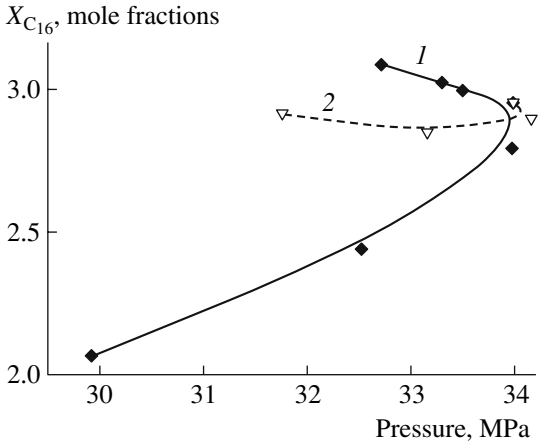

Fig. 3. Hexadecane concentration in mixture 2 vs. pressure in the pore volume of fractionated sand along the line of the gas–(liquid + vapor) phase transition. (*1*) HC mixture input, (*2*) HC mixture recovery.

The second branch *C*"*D*" corresponds to a higher density of the mixture (>300 kg/m^3). In this case, the adsorption capacity of the fine-porous medium is insufficient to sorb all the heptane. Consequently, the three-component (methane–propane–heptane) mixture depleted in heptane; propane (as compared to the starting mixture) is retained, and the phase transition in the three-component mixture is observed.

Fragment *B*"*C*", which is transitional from phase transformations in binary (methane–propane) mixtures to phase transformations in three-component (methane–propane–heptane) mixtures, corresponds to the field of low experimental resolution (Fig. 1, dotted line).

To establish the influence of the molecular mass of the mixture on the phase behavior of the fluid concentrated in the porous medium, the high-boiling component (heptane) in the three-component starting mixture is replaced by a still higher boiling component (hexadecane). The studies were carried out using fractionated sand with an average grain size of 31.5 μm. The composition of weighted three-component mixtures is given in the table (mixture 2). Figure 2 demonstrates phase diagrams of weighted hydrocarbon mixture 2 in the free volume and porous medium. One can see that this mixture, like mixture 1, is characterized by a quantitative transformation of the phase diagram, which occurs in the porous medium compared to the free volume. The boundary curve in the porous volume of sand is shifted toward pressure values lower by 4–5 MPa at temperatures of 420–430 K and by 1.5–2 MPa at temperatures of 270–280 K.

The dependence of the composition and quantity of adsorbed and porous phases on pressure was established based on measurements of calorimetric and thermal parameters. The quantity of the adsorbed phase was determined based on measurements of calorimetric parameters along the crystallization line of the studied hydrocarbon mixture (275–277°C) and compared to the results based on the measurement of thermal parameters.

The quantity of the adsorption phase was established on the basis of the measurement of thermal parameters in the following way. We assumed that transformation of the phase diagram is mainly related to the adsorption of hexadecane. Thus, we could determine the quantity of adsorbed hexadecane. For this purpose, we investigated several pseudobinary mixtures. The pseudobinary mixtures were obtained by mixing one pure component (hexadecane) and a binary mixture (methane and propane). In so doing, we fulfilled the condition following from metric properties of the concentration triangle: points corresponding to the composition of the considered solution should lie on one straight line starting from the triangle vertex corresponding to the pure component [7]. The table shows typical compositions of two mixtures (3 and 4). Figure 2 demonstrates their phase diagrams. The mixtures are characterized by a constant proportion of the methane/propane ratio ($79.8C_1 + 20.2C_3$) at different hexadecane contents (4.8 mol % in mixture 1; 3.0 and 2.0 mol % in mixtures 3 and 4, respectively). The results obtained were used to plot the dependence of the hexadecane content in the pore volume of fractionated sand on pressure along the line of the gas–fluid–vapor phase transition. Figure 3 shows differences in the hexadecane concentration in the pore volume of fractionated sand at the input and recovery of the substance (mixture 2). The recovered mixture, as in the case with mixture 1, is relatively enriched with methane and propane (due to adsorption of high-boiling hexadecane). A decrease in pressure and an increase in temperature lead to desorption of hexadecane and growth of its concentration.

To reveal the influence of water on the phase behavior of hydrocarbons, we used mixture 1 and fractionated

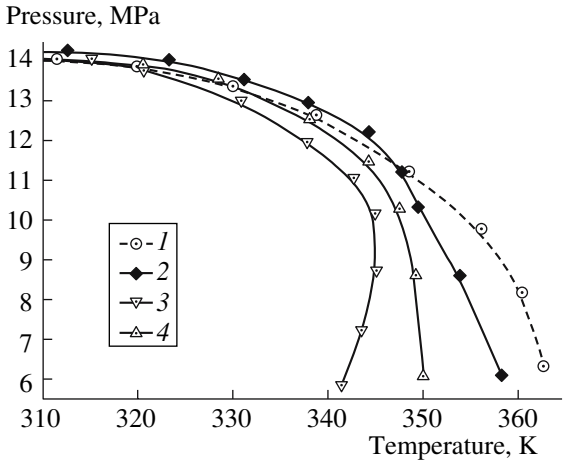

Fig. 4. Phase diagrams of three-component hydrocarbon mixture 1 in the free volume and fractionated sand. (*1*) Free volume; (*2*) sand, 31.5 μm; (*3*) sand, 31.5 μm, water saturation 0.94 vol %; (*4*) the same, water saturation 14.76 vol %.

sand with an average grain size of 31.5 μm. Figure 4 presents phase diagrams of the three-component hydrocarbon mixture in the free volume, dry sand, and water-saturated sand. The content of water was 0.94 and 14.76%. One can see that the boundary curve is shifted by 24.0 K (with respect to the boundary curve in the free volume) at a water content in the pore space equal to 0.94% and pressure equal to 6.0 MPa. This transformation is caused by adsorption of ~40% heptane. With increase in the content of water, adsorption of hydrocarbons decreases, resulting in shift of the boundary curve by ~13.1 K at a content of water equal to 14.76%. This corresponds to adsorption of about 25% heptane.

CONCLUSIONS

The results of our experiments showed that the fine-porous medium noticeably transforms phase diagrams compared to data obtained in the free volume (vessel). The presence of water also changes considerably the physical processes in porous media. The influence of water is manifested to a greater extent in the following way.

Water changes the molecular nature of the porous medium surface and, thus, exerts a significant influence on processes in the bed, including the phase behavior of hydrocarbons.

Being part of the porous medium, water reduces the effective porosity of the collector. Neglect of this fact leads to errors in the estimation of hydrocarbon reserves [8].

Hence, we can draw the following conclusion: despite the importance of experimental analysis of the phase behavior of complex hydrocarbon mixtures in the free volume and water-free porous media, top priority should be given to investigations of porous media with different contents of water.

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