EFFECT OF POROUS MEDIA ON PHASE TRANSITION IN HYDROCARBONS

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The results of an experimental investigation of the condensation of propane, isobutane, butane, and ethane in porous bulk media are given. The presence of the liquid phase is observed at a pressure considerably lower than the saturated-vapor pressure.

There have been many investigations of the effect of porous media on the condensation and evaporation of hydrocarbon systems. The results obtained in different experiments are often contradictory [1-5].

This could be explained by the experimental and methodic difficulties in performing such experiments on multicomponent mixtures with different compositions; accurate determination of changes in the composition of mixtures with a low percentage of heavy hydrocarbons involves considerable difficulties.

We became interested in this problem after examining the results of experiments on the displacement of gaseous propane by carbon dioxide from pipes packed with quartz sand at a pressure close to the saturated-vapor pressure. In these experiments, the amount of propane displaced from the porous medium was much larger than the calculated amount, determined with respect to the measured pressure and the known pore volume of the simulator, which led us to assume the presence of the liquid phase. Sandstone represents most of the gas-bearing rocks. Its adsorptivity with respect to hydrocarbons, which is relatively low, was investigated in a range of pressures remote from the phase-transition pressure. In connection with this, we have investigated experimentally the effect of a porous medium on the phase transitions of chemically pure propane, isobutane, butane, and ethane.

The experiments were performed by means of pipes with a length of 200 cm and diameters of 35 and 50 mm, which were filled with quartz sand of different grain sizes, mixtures of quartz sand and clay powder, and corundum powders. Most of the experiments were performed by using a thermostatically controlled pipe with a length of 198 mm and a diameter of 51 mm, packed with a mixture of quartz sand with grain sizes 0.10-0.25 mm and marshallite dust; both ends of the simulator were sized with a solution of BF-4 paste to a depth of 10-15 mm in order to prevent the loss of dust. The permeability of the simulator, as determined by experiments with nitrogen, was equal to k = 33 millidarcy, while the pore volume was equal to $V_{si} = 720$ cm^3.

The simulator was filled slowly at room temperature with a chemically pure gaseous hydrocarbon. The hydrocarbon was supplied from a thermostated small tank or cylinder, which was first filled with condensate and placed outside the room in a tank containing water; the water was heated in cold weather. After the simulator was filled with the hydrocarbon and the pressure was equalized and stabilized, slow release of gas through a gas counter was effected periodically. The counter readings were recorded during this procedure, and pressure readings at the inlet and outlet sections of the simulator were recorded. The experiments were performed at different initial pressures P_0; they were characterized by the values $\Delta P = P_s - P_0$ and P_0/P_s. In these expressions P_s is the saturated-vapor pressure of the hydrocarbon at the simulator temperature, which, for simulators that are not thermostated, is assumed to be equal to the ambient temperature.

Figure 1 shows typical curves of the amount of gaseous propane contained in the pore volume, which is characterized by P/z, as a function of the quantity of gas Q that has left the thermostated simulator. If the initial pressure differs considerably from the saturated-vapor pressure, this dependence is linear ($\Delta P = 2.58$ tech. atm) or close to linear ($\Delta P = 1.66$ tech. atm).

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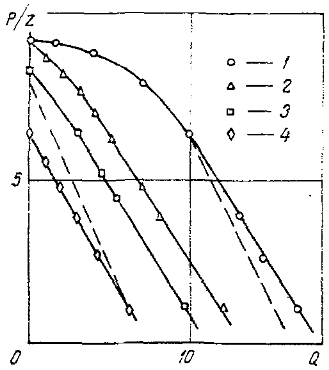

Fig. 1

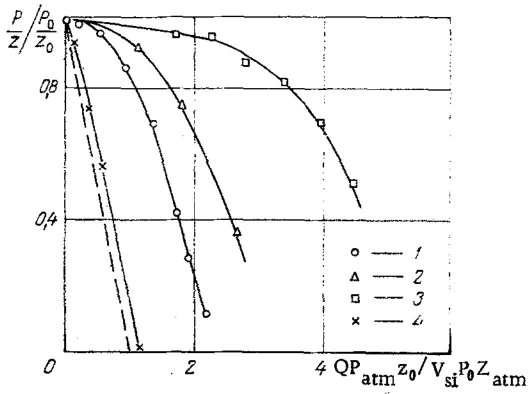

Fig. 2

Fig. 1. Dependences $P/z = f(Q)$ for propane in the thermostated simulator ($k = 33$ millidarcy). 1) $\Delta P = 0.44$ tech. atm; 2) 0.9; 3) 1.66; 4) 2.58. The dashed curve pertains to nitrogen; P/z is given in absolute atmospheres.

Fig. 2. Dependences $(P/z)/(P_0/z_0) = f(QP_{atm} z_0/V_{si} P_0 a_{atm})$ for propane, isobutane, butane, and ethane in the thermostated simulator for $P/P_s = 0.94$. 1) Propane, $\Delta P = 0.44$ tech. atm; 2) isobutane, $\Delta P = 0.176$ tech. atm; 3) butane, $\Delta P = 0.13$ tech. atm; 4) ethane, $\Delta P = 2.73$ tech. atm.

At a pressure close to the saturated-vapor pressure ($\Delta P = 0.44$ tech. atm), the escape of gas from the simulator produces a slight pressure drop at the initial stage, after which the pressure variation is approximately linear. In these cases, the amount of propane that has escaped is always larger than the amount that the pore volume can contain in the gaseous state. This indicates that the pore volume contains liquid or sorbed propane, which evaporates as the pressure drops with the escape of gas. After the release of the next hydrocarbon batch, a certain increase of the mean pressure in the simulator is observed over a period of time, which also indicates that hydrocarbon evaporation or desorption takes place.

We have also recorded the $P/z = f(Q)$ dependence for the thermostated simulator, filled with isobutane, butane, and ethane. For the sake of comparison, these dependences as well as the dependence obtained for propane are plotted in terms of relative quantities,

$$\frac{P/z}{P_0/z_0} = f\left(\frac{QP_{atm}z_0}{V_{si}P_0z_{atm}}\right),$$

and are shown in Fig. 2. The measure of the effect a porous medium exerts on phase transition is determined by the physicochemical characteristic of the hydrocarbon.

The quantities measured experimentally can be used for calculating the part of the pore volume occupied by the liquid (saturation s):

$$s = \frac{G_\Sigma - G_g}{V_{si}\rho_l}.$$

The total amount of hydrocarbon in the simulator is $G_\Sigma = (Q + V_{si})\rho_{atm}$. The amount of gaseous hydrocarbon in the simulator is equal to $G_g = V_{si}(1 - s)\rho_{P,t}$, where V_{si} is the pore volume of the simulator, Q is the amount of gas that has left the simulator with an allowance for sorbed gas, ρ_{atm} and $\rho_{P,t}$ are the values of the hydrocarbon density under atmospheric conditions and at the initial pressure and temperature, respectively, and ρ_l is the density of the liquid hydrocarbon on the saturation curve. After substituting the expressions for G_Σ and G_g, we obtain

$$s = \frac{Q\rho_{atm} - V_{si}(\rho_{P,t} - \rho_{atm})}{V_{si}(\rho_l - \rho_{P,t})} \qquad (1)$$

(the method of determining the amount of sorbed gas is described below). For comparing the phase transitions of different hydrocarbons, one should use the quantity $a = s\rho_l$, which expresses the mass of the liquid-phase substance per unit pore volume.

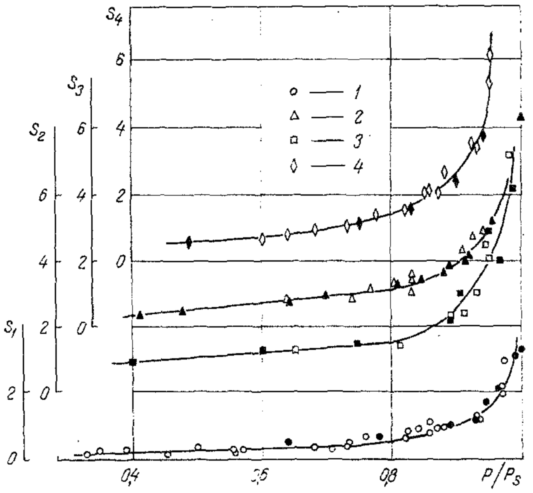

Fig. 3

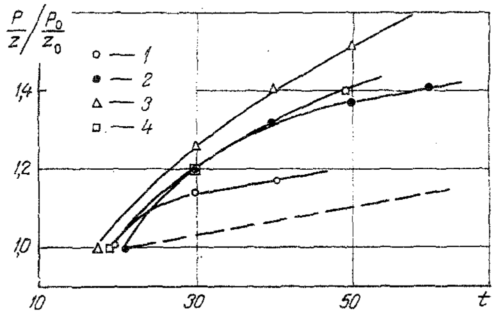

Fig. 4

Fig. 3. Dependence $s = f(P/P_s)$ for ethane (1), propane (3), isobutane (2), and butane (4) for the thermostated simulator (k = 33 millidarcy). The black points pertain to $P_0 = P_s$; the white points pertain to $P_0 < P_s$.

Fig. 4. Dependences $(P/z)/(P_0/z_0) = f(t)$ for propane, isobutane, and butane for the thermostated simulator. 1) $\Delta P = 0.66$ tech. atm; 2) 0.25 tech. atm, propane; 3) 0.144 tech. atm, isobutane; 4) 0.25 tech. atm, butane. The temperature t is given in degrees Celsius.

Figure 3 shows the dependences $s = f(P/P_s)$, plotted on the basis of the experimental results for different initial pressures. These dependences show that, in the pore volume, the liquid hydrocarbon is present at a pressure much lower than the saturated-vapor pressure, while its quantity increases sharply in approaching the saturation pressure. For instance, a saturation $s = 1\%$ for propane occurs even if $P/P_s = 0.5$, while $s = 3.95\%$ if $P/P_s = 0.95$.

The amount of liquid phase as a percentage of the total hydrocarbon quantity contained in the pore volume σ can be determined by means of the expression $\sigma = V_{si} s \rho_l / (Q + V_{si}) \rho_{atm}$; for instance, for propane and $s = 1\%$, $\sigma = 35\%$.

The gradual increase in saturation by the liquid hydrocarbon when the pressure approaches the saturated-vapor pressure allows us to state that phase transition in a porous medium cannot be characterized by a definite pressure value.

The dependence $s = f(P/P_s)$, determined for different $\Delta P > 0$, represents the adsorption isotherm. If, during the filling of the porous medium, the pressure has reached the saturated-vapor pressure or has exceeded it, $\Delta P = 0$ at the beginning of the release process, and the dependence $s = f(P/P_s)$ represents the desorption isotherm, which may be located above the adsorption isotherm because of hysteresis in capillary condensation. Figure 3 shows that the values of saturation of the thermostated simulator with the liquid hydrocarbon virtually coincide in experiments with the initial values $\Delta P > 0$ and $\Delta P = 0$. Hysteresis is not observed, which indicates the absence of micropores.

For initial pressures differing considerably from the saturated-vapor pressure, when the linear dependence $P/z = f(Q)$, which seems to correspond to gas depletion conditions, holds, calculation of the degree of saturation yields $s > 0$. The cause of this becomes clear if we compare the slopes of the dependence $P/z = f(Q)$ for propane and for nitrogen (dashed curve in Fig. 1). By writing the equation of state for the gas for the initial pressure value P_0 and the present value P and subtracting the second equation from the first, we obtain

$$\frac{P}{z} = \frac{P_0}{z_0} - \frac{P_{atm}}{V_{si} z_{atm}} Q,$$

where P_{atm} is the atmospheric pressure and z_{atm} is the compressibility factor under atmospheric conditions.

The slope of the straight line described by Eq. (2) with respect to the axis of abscissas is determined by the value of $P_{atm}/V_{si} z_{atm}$.

Since $z_{atm} = 1$ for nitrogen and $z_{atm} < 1$ for propane,

$$\left(\frac{P_{\mathrm{atm}}}{V_{si} z_{\mathrm{atm}}}\right)_{pr} > \left(\frac{P_{\mathrm{atm}}}{V_{si} z_{\mathrm{atm}}}\right)_{ni}$$

and the straight lines $P/z = f(Q)$ should have a larger slope with respect to the Q axis for propane than for nitrogen. Actually, the opposite takes place. The fact that the slope of decrease in P/z along the linear part of the dependence $P/z = f(Q)$ during the release of propane from the simulator is milder than would be indicated by the equation of state for the gas can be explained by an increase in the amount of gaseous propane as a result of desorption with a drop in pressure. The quantity of propane desorbed with a reduction in pressure to atmospheric pressure can be estimated on the basis of the following considerations. For example, consider the point with the coordinates Q = 10 liters and P/z = 6.35 on the linear part of the dependence $P/z = f(Q)$ for $\Delta P = 0.44$ tech. atm (see Fig. 1). This point corresponds to P = 5.51 abs. atm and t = 17.6°C. As the pressure drops to atmospheric pressure, $\Delta Q = 16.7-10 = 6.7$ liters of propane escapes from the simulator. If we draw from the initial point a straight line parallel to the line characterizing the variation of nitrogen pressure, we obtain $\Delta Q = 15.2-10 = 5.2$ liters. The additional amount of propane that has escaped from the simulator as the pressure drops from P = 5.51 abs. atm to atmospheric pressure is equal to $z_{\mathrm{atm}} = 0.955$, which amounts to $(6.7-5.2)/0.955 = 1.57$ liters, $1570\ \mathrm{cm}^3/8250\ \mathrm{g} = 0.19\ \mathrm{cm}^3/\mathrm{g}$ per unit weight of sorbent. We can similarly determine the amount of gas desorbed with the atmospheric pressure dropping to zero, which is necessary for accurate calculations of the degree of saturation.

The described procedure can serve as a methodic base for determining the sorption ability of different porous media.

The two-phase state of a hydrocarbon in a porous medium at pressures lower than the saturated-vapor pressure is clearly illustrated by the heated simulator experiment. The simulator is filled with a gaseous hydrocarbon to a pressure $P < P_s$ and is then slowly heated by means of the thermostat and then kept at a certain temperature until the pressure gauge readings are stabilized. Figure 4 shows the relative variation of P/z as a function of the simulator temperature in experiments with propane at the initial values $\Delta P = 0.25$ tech. atm and $\Delta P = 0.66$ tech. atm, isobutane at $\Delta P = 0.144$ tech. atm, and butane at $\Delta P = 0.26$ tech. atm. A dashed straight line describing the relative variation of $P/z = f(t)$ for a constant amount of gaseous substance according to the isochoric law ($P/z \sim T$) is drawn from the point on the diagram that characterizes the initial gas parameters in the simulator. The experimental curves in Fig. 4 indicate that a rise in the simulator temperature first causes a sharp increase in pressure, after which the variation of pressure approaches isochoric behavior. The sharp pressure rise in the simulator with an increase in temperature can be explained by evaporation and desorption processes, which manifest themselves the more strongly, the smaller the initial value of ΔP.

Propane condensation was investigated by using a number of simulators with different porous media. In a homogeneous simulator with relatively good permeability, filled with quartz sand of 0.2-0.25-mm grain size (k = 24 darcy), condensation phenomena are not very strongly pronounced, and s = 1% at $P/P_s = 0.99$ ($\Delta P = 0.1$ tech. atm). In a homogeneous simulator with lower permeability, filled with quartz sand of 0.1-0.2-mm grain size (k = 12 darcy), these phenomena are more strongly pronounced, and s = 1% at $P/P_s = 0.6$ ($\Delta P = 3.1$ tech. atm. In a simulator filled with a low-permeability mixture of sand with wide-range grain sizes and marshallite (k = 18 millidarcy), the condensation phenomena are pronounced most strongly, and s = 1% at $P/P_s = 0.5$ ($\Delta P = 3.9$ tech. atm). Experiments with the same sand mixture freely poured into the pipe without compacting have shown that, for equal values of P/P_s, the degree of saturation decreases in proportion to the reduction of the amount of rock in the simulator, which indicates that the total surface of the porous medium plays a decisive role in phase transition phenomena.

Sorption and condensation of propane were also observed in experiments on simulators packed with a mixture of sand and 25% dry or moist bentonite clay as well as in simulators packed with a corundum powder.

For the various above-mentioned porous media, the amount of desorbed propane varied in the range 0.3-1.2 cm^3/g with a reduction in pressure from 5 abs. atm to 1 abs. atm.

In the thermostated simulator, the amount of sorbed matter in the relative pressure range from $P/P_s = 0.5$ to $P/P_s = 0.8$ at room temperature is equal to 0.13 cm^3/g for ethane, 0.15 cm^3/g for propane, 0.21 cm^3/g for butane, and 0.18 cm^3/g for isobutane. These amounts correspond approximately to the changes in the values of the empirical parachor function for the above hydrocarbons.

Similar sorption and condensation phenomena in the thermostated simulator were also observed when the latter was filled with a mixture of propane and 5.46% pentane.

Using a simulator with $k = 18$ millidarcy, we also performed experiments to determine the effect of a porous medium on the phase transitions of propane in a mixture with a small amount (10-15%) of nitrogen or carbon dioxide. The presence of an inert gas does not affect the above-mentioned phase transitions at partial pressures lower than the saturated-vapor pressure.

In addition to the generally accepted parameters — the porosity, permeability, the particle size distribution curve, and the porometric curve — a porous medium can probably be characterized also by the experimental dependence $s = f(\Delta P)$ or $s = f(P/P_s)$, determined for a certain gas which is readily sorbed.

The above results of the experimental investigation of the effect of porous media on the phase transitions of individual hydrocarbons in the region of direct condensation cannot be used to characterize the processes of retrograde condensation of hydrocarbon mixtures.

NOTATION

P, pressure; P_s, saturated-vapor pressure; ρ, density; V_{si}, pore volume of the simulator; z, compressibility factor; G, quantity of matter; Q, gas volume; s, saturation; σ, weight percentage of the liquid phase; T, t, absolute temperature and temperature in degrees Celsius, respectively; R, gas constant; a, amount of desorbed matter; k, permeability.

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HEAT AND MASS TRANSFER IN UNDEVELOPED BOILING IN HEAT-TRANSMITTING SLOT CHANNELS

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One of the variants of the problem of thermostatic control of objects involving quasistationary boiling of a heat-transfer medium in capillary gaps is examined.

In [1, 2] we considered the problem of the temperature control of some objects heated unilaterally by radiation by the use of narrow heat-transmitting channels filled with a subliming heat-transfer medium and obtained equations for engineering calculations of their optimum geometric characteristics.

In the case where the heat regime of operation of such devices is altered and the thermodynamic parameters of the medium are above the triple point, they can function as ordinary heat pipes in which effective heat conduction is obtained by a double phase change and return of the liquid phase to the evaporation zone. The role of the wick in this case is played by the closed slot channels partially filled with liquid. On the heat-receiving region of the channel walls vapor bubbles will arise and will grow. The breakaway of the bubbles

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