The calculation of the phase equilibrium of the multicomponent hydrocarbon systems

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Abstract. Hydrocarbon mixtures filtration process simulation development has resulted in use of cubic equations of state of the van der Waals type to describe the thermodynamic properties of natural fluids under real thermobaric conditions. Binary hydrocarbon systems allow to simulate the fluids of different types of reservoirs qualitatively, what makes it possible to carry out the experimental study of their filtration features. Exploitation of gas-condensate reservoirs shows the possibility of existence of various two-phase filtration regimes, including self-oscillatory one, which occurs under certain values of mixture composition, temperature and pressure drop. Plotting of the phase diagram of the model mixture is required to determine these values. A software package to calculate the vapor–liquid equilibrium of binary systems using cubic equation of state of the van der Waals type has been created. Phase diagrams of gas-condensate model mixtures have been calculated.

1. Introduction
Gas-condensate fields are of particular interest among the various types of hydrocarbon fields. One has to deal with products that change their compositions constantly during developing such fields. Such behavior of the formation fluid can be explained by the phenomenon of the retrograde condensation of the hydrocarbon mixture that occurs when the formation pressure decreases. As soon as pressure in the formation decrease below dew point pressure, the high-molecular hydrocarbon components of the mixture start to transit into liquid phase, which remains immobile practically throughout the development of the field due to low phase saturation. In this case further pressure reduction leads to an increase in the fraction of the liquid phase until the pressure reaches the maximum condensation pressure.

The phenomenon of retrograde condensation is explained by the presence of the interaction forces between the molecules. The liquid phase can exist at a pressure exceeding the saturated vapor pressure of the substance and at a temperature below critical one. If the first condition is not observed the forces between molecules are too weak because of the substantial distances between them, so the liquid phase is not formed. If the second one is not observed, than kinetic energy of the molecules is too great to ensure the presence of liquid phase. Retrograde properties appear under high pressure, they can be explained by the interaction forces between light and heavy molecules: the gas phase becomes dense enough for the light molecules in it to draw heavy molecules from liquid phase [1].

Accurate and low-cost methods for describing the phase behavior of hydrocarbon systems is required to improve the quality oil and gas-condensate fields design and operation, to determine
optimal conditions for field processing, transportation and refining raw material. Calculating phase equilibrium of a multicomponent hydrocarbon system using equation of state is the most convenient approach since the equation contains the whole information about the given system in compact analytical form.

Previously, it was shown that the occurrence of different filtration regimes of hydrocarbon mixtures is possible [2,3]. In this relation, it is necessary to prepare a model mixture to conduct adequate physical simulation of the filtration process, so the calculation of the exact fractions of the components is needed to obtain a mixture with the required properties. In this work, a software package to calculate the phase equilibrium of the multicomponent hydrocarbon systems containing hydrogen sulfide, carbon dioxide and nitrogen in their composition has been developed for this purpose.

The paper describes an approach to model multicomponent mixtures with phase transitions, which is of a practical importance also for studying the equations of state of organic compounds at high energy densities [4] as well as the non-congruent phase transitions in plasmas [5].

2. Algorithm

The problem is set up as follows: the component composition of the mixture, mole fractions of the components \( \eta_i \) \( (i = 1, \ldots, N) \), pressure \( P \) and temperature \( T \) are given. It is required to determine the mole fractions \( V \), \( L \) and the composition of the vapor \( y_i \) and liquid \( x_i \) phases into which the initial mixture segregates for a given thermobatic conditions. Thus, it is required to determine the values of \( 2N + 2 \) variables.

The corresponding \( 2N + 2 \) equations have the following form:

\[
\begin{align*}
    f_{Li} - f_{V_i} &= 0, \\
    x_iL + y_iV - \eta_i &= 0, \\
    \sum_{i=0}^{N} y_i - 1 &= 0, \\
    L + V &= 1.
\end{align*}
\]

In this system of (1)–(4), the first \( N \) equations correspond to the conditions of thermodynamic equilibrium—the equality of the fugacities \( f_{V_i} \) and \( f_{Li} \) of the components in the coexisting vapor and liquid phases. The following \( N \) equations describe the material balance of the components in the phases. Fugacity \( f \) can be defined as the pressure that a given real system must produce in order to have the same effect as an ideal system [6]. It characterizes the deviation from the ideal state and, like the pressure for an ideal gas, can be considered as a measure of the dispersibility of matter—the aim of the latter to occupy a larger volume.

The equation of state of the van der Waals type developed especially for natural oil and gas-condensate mixtures for pressures up to 100 MPa and temperatures up to 473 K by Brusilovsky is used to calculate the vapor–liquid equilibrium of a multicomponent system [7]:

\[
p + \frac{a}{(v + c)(v + d)} = \frac{RT}{(v - b)},
\]

where \( p \) is the pressure, \( v \) is the specific volume, \( T \) is the temperature, \( R \) is the universal gas constant, \( a, b, c, d \) are the coefficients, the coefficient \( a \) depends on the temperature \( T \), the coefficients \( b, c, d \) are independent.

It is required to know the following data for each component of the mixture under consideration: the critical temperature \( T_c \), the critical pressure \( P_c \), the Pitzer’s acentric factor \( \omega \) and the three parameters of the equation of state—\( \Omega_c, Z'_c, \psi \) and the coefficients of pair interaction with other components and the accuracy of the calculation. There are tabular values of \( \Omega_c, Z'_c \) and \( \psi \) for some components and they are functions depend on \( \omega \) for another ones [7].
The described parameters of the equation of state were calculated from the experimental data. Then it is possible to calculate the values of coefficients $a$, $b$, $c$, $d$ for each pure component:

$$a_i = a_{ci}\phi_i(T),$$  \hspace{1cm} (6)  

$$b_i = \beta_i\frac{RT_{ci}}{P_{ci}},$$  \hspace{1cm} (7)  

$$c_i = \sigma_i\frac{RT_{ci}}{P_{ci}},$$  \hspace{1cm} (8)  

$$d_i = \delta_i\frac{RT_{ci}}{P_{ci}},$$  \hspace{1cm} (9)  

where

$$a_{ci} = \alpha_i\frac{R^2T_{ci}^2}{P_{ci}},$$  \hspace{1cm} (10)  

$$\phi_i(T) = \left[1 + \psi_i \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2,$$  \hspace{1cm} (11)  

$$\alpha_i = \Omega_{ci}^3,$$  \hspace{1cm} (12)  

$$\beta_i = Z'_{ci} + \Omega_{ci} - 1,$$  \hspace{1cm} (13)  

$$\sigma_i = -Z'_{ci} + \Omega_{ci}(0.5 + \sqrt{\Omega_{ci} - 0.75}),$$  \hspace{1cm} (14)  

$$\delta_i = -Z'_{ci} + \Omega_{ci}(0.5 - \sqrt{\Omega_{ci} - 0.75}).$$  \hspace{1cm} (15)  

The equation of state for the mixture has the same form as for the pure components. In this case, the coefficients of the equation of state of a multicomponent system are determined by the properties of the components forming the mixture and the fraction of each one in the mixture.

The calculation is carried out by an iterative method while the following condition for each component is true:

$$\frac{f_{li}}{\sqrt{V_i}} - 1 > \varepsilon,$$  \hspace{1cm} (16)  

where $\varepsilon$ is the accuracy of observing the equality of fugacities for each component.

### 3. Results

Figure 1 shows typical phase diagram of the gas-condensate model mixture, which was calculated using algorithm described above. There is a boundary of the retrograde area at the figure, and
an occurrence of self-oscillatory filtration regime [3] is possible, if inlet pressure is above dew point curve and outlet pressure is below boundary of the retrograde area.

Figures 2 and 3 show comparison of calculated two-phase boundary with experimental data [8]. There is a difference between calculated boundary of two-phase area and experimental one near critical point, but this accuracy is high enough for determination of pressure drop, which leads to changing filtration regimes.
4. Conclusions
Software package to calculate the vapor–liquid equilibrium of multicomponent systems via cubic equation of state of the van der Waals type has been created. This approach allows determinate parameters of the filtration process of model mixtures to receive various filtration regimes including self-oscillatory one.

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References
[1] Lapshin V I, Volkov A N and Kinstonnov A A 2014 Vesti Gazovoy Nauki 18(2) 120–8
[2] Direktor L B, Kachalov V V, Maikov I L and Skovorod’ko S N 2000 One-dimensional non-stationary model of two-phase filtration of gas-condensate mixture Preprint 2 (Moscow: JIHT RAS)
[3] Kachalov V V, Maikov I L, Molchanov D A and Torchinskiy V M 2014 Vesti Gazovoy Nauki 18(2) 106–12
[4] Bushman A V, Lomonosov I V, Fortov V E and Khishchenko K V 1994 Khim. Fiz. 13(5) 97–106
[5] Stroev N E and Iosilevskiy I L 2016 J. Phys.: Conf. Ser. 774 012040
[6] Prigogine I and Defay R 1954 Chemical Thermodynamics (London: Longmans, Green & Co)
[7] Brusilovsky A I 2002 Phase Transitions in the Development of Oil and Gas Reservoirs (Moscow: Graal)
[8] Kogan V B, Fridman V M and Kafarov V V 1966 Liquid–Vapor Equilibrium vol 1 (Moscow: Nauka)