Modeling the effect of dynamic adsorption on the phase behavior of hydrocarbons in shale and tight reservoirs

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Abstract. It is known that in shale and tight reservoirs, adsorption significantly affects hydrocarbon reserves and the processes of their production. This fact is reflected in the methods for calculating reserves and evaluating the production potential of shale and tight deposits. To calculate the initial content of the components, multi-component adsorption models are used. The impact on hydrocarbon production is taken into account through special dynamic permeability models for shale reservoirs. According to laboratory studies, adsorption can lead to significant changes not only in volume, but also in the composition of the produced fluids and their phase behavior. Previously, this effect could not be reproduced on the basis of mathematical models. The method proposed in this article allows modeling the phase behavior of a hydrocarbon mixture taking into account the dynamic adsorption/desorption of components in the process of pressure change. The method is applicable in the simulations of multi-component (compositional) flow and PVT-modeling of real reservoirs. The phase behavior of hydrocarbons with pressure depletion in shale reservoirs has been simulated. It is shown that neglecting the dynamic effect of adsorption/desorption leads to significant errors in predicting the saturation pressure, as well as the dynamics of changes in the composition of the produced fluid and of hydrocarbon component recovery.

Keywords: phase behavior, oil, gas, multicomponent hydrocarbon mixture, multicomponent adsorption, shale reservoir, numerical algorithm

Introduction

Studies of the phase behavior of multicomponent hydrocarbon mixtures are an integral part of the theory and practice of modeling, designing and analyzing the development of oil and gas condensate deposits. In theoretical terms, their most important element is the calculation of phase equilibrium – the problem of determining the number, fractions and compositions of the phases into which the hydrocarbon mixture is divided under given thermobaric conditions. Phase equilibrium calculations are of particular importance in multicomponent (compositional) flow simulations used to design and evaluate technological solutions in the development of oil and gas condensate deposits with intensive interfacial mass transfer (Aziz, Wong, 1989; Coats, 1998). They are also the basis for PVT-modeling (PVT – pressure-volume-temperature) used for creating reservoir fluid models (Whitson, Brule, 2000) and their matching to data of laboratory experiments on fluid samples in bulk (PVT cells) (Pedersen, Christensen, 2006).

In oil and gas deposits, a number of factors can lead to significant deviations of the actual phase behavior of the reservoir hydrocarbon mixture from that observed in the study of samples in bulk. As a result, during the development of the field there is a discrepancy between the measured and predicted data. Such factors include the influence of water (Buleiko et al., 2007), trapped hydrocarbons (Brusilovskii, 2002), rock surfaces (Buleiko et al., 2007; Pang et al., 2013), capillary pressure (Nojabaei et al., 2013; Shapiro, Stenby, 2001), etc.

It is well known that in shale and tight reservoirs a great influence on hydrocarbon reserves and the dynamics of their production is exerted by the adsorption/desorption of the components of formation fluids (Zendehboudi, Bahadori, 2015). Experimental studies show that adsorption can also have a significant impact on the composition of the hydrocarbon mixture and its phase envelope (Buleiko et al., 2007).

Experimental determination of the amount of adsorbed substance (adsorption isotherms) for methane,

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ethane, nitrogen and other components, as well as binary and multicomponent mixtures, on various adsorbents in a wide range of temperature and pressure conditions has been studied by many authors. Choi et al. (2003) studied the pure component adsorption of methane, ethane, ethylene, nitrogen, and oxygen on activated carbon. However, the pressure in the experiments did not exceed 2 MPa, which is significantly lower than the typical reservoir pressures. The adsorption isotherms presented by (Song et al., 2007) for pure components on zeolite indicate that the pore structure of even the same adsorbent can have a significant effect on the adsorption behavior, especially for hydrocarbons heavier than C_5. Luo et al. (2015) considered adsorption of not only pure components, but also their mixtures, and Wang et al. (2015) studied adsorption of methane-ethane mixtures in different proportions. It was shown that the ratio of the components of the mixture significantly affects the intensity of their adsorption. Yun et al. (2002) also studied methane, ethane, and their binary mixtures, but on the MCM-41 adsorbent, which is characterized by a chemically homogeneous pore surface and simple pore structure. In (Matsumoto et al., 1997) it was shown that Langmuir model provides a good approximation for the adsorption isotherms of the heavy components on activated carbon for pressures up to 0.1 MPa. However, this is not true for higher pressures (Dong et al., 2016).

Despite the fact that the adsorption of hydrocarbons in shales has been intensively studied in the last decade, considerable attention has not been paid to modeling the influence of adsorption on the dynamic changes in the composition of hydrocarbon mixture and its phase behavior. The study (Ambrose et al., 2011) provides an example of calculating the geological reserves (volumes-in-place) of shale gas, taking into account the difference in the composition of free gas and adsorbed fluid for a five-component model of a hydrocarbon mixture in a shale reservoir. Dong et al. (2016) and Sandoval et al. (2016) developed similar methods of taking into account multicomponent adsorption in calculations of the phase behavior of hydrocarbons. It is assumed that adsorption affects phase equilibrium by changing the effective radii of pores due to the formation of thin adsorption films on the surface of rocks, which leads to minor changes in capillary pressure. The work (Dong et al., 2016) also considers the shift of the critical point of mixture caused by adsorption. The results of both studies showed a practically insignificant effect of taking adsorption into account, despite the fact that the effect of capillary pressure in a porous medium on the phase behavior of fluids was significant. In both papers, the effect of dynamic adsorption/desorption on the fluid composition in pores with a change in pressure was not studied.

The article (Sandoval et al., 2018) presents an alternative algorithm for calculating the phase equilibrium of a hydrocarbon mixture (the so-called flash-algorithm), taking into account multicomponent adsorption and capillary pressure in pores. The authors established a significant impact of these factors on the phase envelope and the calculated compositions of hydrocarbon phases. They introduce a hypothetical "excess adsorbed phase" in phase behavior calculations which is not a real thermodynamic object. It reflects compositional difference of the real adsorbed phase from the bulk part of the mixture, for which the equilibrium calculation of fractions and compositions of the vapor and liquid phases is performed. Integral compositional balance includes the bulk part of the mixture in the total pore volume and the "excess adsorbed phase" in the volume occupied by the adsorbed substance. The results obtained are in qualitative agreement with known field and experimental data. However, the use of the proposed model for practical applications is highly complicated by the need to obtain a large amount of initial data for a multicomponent adsorption model in a real reservoir, which is heterogeneous in lithology, pore structure, physico-chemical characteristics, etc.

This article also presents a method for taking into account dynamic changes in the composition due to the adsorption/desorption of components when modeling the phase behavior of hydrocarbon mixtures in tight and shale reservoirs. The iterative algorithm differs from the one presented in (Sandoval et al., 2018), but also uses a multicomponent adsorption model to obtain the adsorbed amount of each component, and further use of the current composition of the "free fluid" in phase behavior calculations under given temperature and pressure conditions. To take into account the heterogeneity of real reservoir properties, such as porosity, specific surface area of pores, etc., a special control parameter has been introduced in the model. It has a certain physical meaning and can be measured experimentally for a real heterogeneous reservoir. On the other hand, if laboratory data for a specific heterogeneous reservoir are insufficient, adjustment of this parameter (e.g., by matching of the adsorbed fraction of fluid at initial reservoir conditions) provides an equivalent model which can be used in phase behavior calculations. This makes the method much more convenient in practical calculation for real deposits.

The developed method is illustrated by calculations of the phase behavior of a hydrocarbon mixture during the dynamic desorption of components caused by a decrease in pressure during the depletion of a deposit. A significant effect is shown of adsorption/desorption processes on the saturation pressure, as well as on the dynamics of the phases' composition.

In subsequent sections of the article, the model and computational algorithm are first described. Then their application is illustrated by the example of a multicomponent hydrocarbon mixture and the results obtained are discussed.

Mathematical model

In this section, we describe a model and a general computational algorithm that includes blocks for calculating phase equilibrium and dynamic multicomponent adsorption.

Phase equilibrium

The key assumption of the model is that the phase behavior of the hydrocarbon mixture during component adsorption by the reservoir surface can be described in the same way as in bulk. But it is necessary to take into account the change in the total composition of the "free part" of the mixture due to the adsorption/desorption of individual components. This assumption arose from the analysis of experimental data (Buleiko et al., 2007). Other possible effects of a porous medium, such as pressure differences between phases (capillary pressure in pore channels with regard to adsorption films) and the shift of a critical point, can be included in the model by analogy with the works (Dong et al., 2016; Sandoval et al., 2016; Sandoval et al., 2018). In this paper, they are not taken into account in order to emphasize the effect on the phase behavior of the dynamic change in the total composition of the mixture due to the adsorption/desorption of components.

The equilibrium of the vapor and liquid phases at a given pressure, temperature and total mixture composition is determined by the equality of chemical potentials for each component between the phases (Brusilovskii, 2002; Whitson, Brule, 2000):

$$\mu_{i,L} = \mu_{i,V}, \quad i = 1,..,N, \qquad (1)$$

where i is the component index of the mixture; N is the total number of components in the mixture; μ_i is the chemical potential of component i; the subscripts L and V denote the liquid and vapor phases, respectively.

In terms of fugacities, equation (1) takes the form:

$$lnf_{i,L} = lnf_{i,V}, \quad i = 1,..,N \qquad (2)$$

The fugacities of the components in the vapor and liquid phases can be found by the known thermodynamic relations based on the solution of the equation of state (EOS). In oil and gas applications, the Peng-Robinson cubic equation of state (Peng, Robinson, 1976) with the three-parameter modification (Jhavery, Youngren, 1988) has received the most distribution:

$$p = \frac{RT}{v-b} - \frac{a}{(v+c)(v+d)}, \qquad (3)$$

where v is the molar volume of the phase; a is a coefficient depending on temperature T; b, c and d are constant coefficients. Usually, equation (3) is rewritten to the cubic form:

$$v^3 + \left(c + d - b - \frac{RT}{p}\right)v^2 + \left(\frac{a}{p} - bc + cd - bd - \frac{RTd}{p} - \frac{RTc}{p}\right)v - \left(bcd + \frac{RTcd}{p} + \frac{ab}{p}\right) = 0. \qquad (4)$$

The acentric factor ω_i, critical pressure P_{ci} and temperature T_{ci} for each component i, as well as the binary interaction coefficients of the components, are used to calculate the coefficients a, b, c and d in equation (4) for a given phase composition. Further, equation (4) is solved with respect to the z-factor $z = \frac{pv}{RT}$. The z-factor of the phase is then used to calculate the component fugacities (Brusilovskii, 2002).

Equations (2) must be supplemented by normalization constraints. The final system of algebraic equations for determining the fractions and compositions of the equilibrium phases is:

$$\begin{cases} lnf_{i,L} - lnf_{i,V} = 0, \quad i = 1,..,N \\ x_i L + y_i V - z_i = 0, \quad i = 1,..,N \\ \sum_{i=1}^{N} y_i - 1 = 0 \\ L + V = 1 \end{cases} \qquad (5)$$

Determination of the equilibrium molar fractions of L and V and the compositions (molar concentrations of the components) y_i and x_i of the vapor and liquid phases based on system (5) given the total composition of the mixture z_i, pressure p and temperature T is called the phase equilibrium problem, or the "flash" problem. To solve it, a number of methods are used, among which the method of successive substitutions, the Newton method and their modifications are most common (Michelsen, 1982 (a); Brusilovskii, 2002). These iterative procedures include solving the Rachford-Rice equation for V (Whitson, Brule, 2000):

$$F(V) = \sum_{i=1}^{N} \frac{z_i(K_i-1)}{V(K_i-1)+1} = 0, \qquad (6)$$

where $K_i = \frac{y_i}{x_i}$ are the K-values (equilibrium constants). Initial estimates for K_i can be found from the Wilson correlation

$$K_i = \frac{P_{ci}}{P} exp\left[5{,}373(1 + \omega_i)(1 - \frac{T_{ci}}{T})\right] \qquad (7)$$

or obtained using phase stability analysis (Michelsen, 1982 (b)). If the phase equilibrium calculations are repeated for varying temperature and pressure conditions, then initial approximations for K_i can be obtained from the solution found at previous pressure/temperature values.

The described procedure is widely used in calculations of the phase behavior of hydrocarbon mixtures as applied to the modeling and design of field development. Nonessential changes can be introduced to the system of equations (5) to take into account capillary pressure (Brusilovskii, 2002; Sandoval et al., 2016) and some other features of the porous medium (Dong et al., 2016).

In the proposed method, taking into account the adsorption of components, the novelty in the described procedure is that z_i in system (5) is not the total composition of the hydrocarbon mixture in the element of the porous medium, but the composition of free (not adsorbed) part of it. As compared to (Sandoval etc., 2018), only the composition z_i of the free part of the mixture is used in calculations, while its volume and density are not involved, and "excess adsorbed phase" is not required. We describe these differences in more detail below.

One more feature is also important to be noted. Using the composition z_i of the free part of the mixture in phase equilibrium calculations is not equivalent to adopting a constant composition of the mixture in accordance with the ideally collected sample of the initially free formation fluid and performing further calculations using standard procedures. The proposed method takes into account that in the conditions of field development the composition of free part of the hydrocarbon mixture changes continuously due to dynamic adsorption/ desorption of components.

Multicomponent adsorption

In publications, one can find a rather large amount of experimental data on the adsorption of individual hydrocarbons on various adsorbents. However, most of these results were obtained either at too low pressures or on industrial adsorbents, and therefore are not suitable for direct application to oil and gas reservoirs. The exception is methane, due to worldwide interest in its reserves in coal beds and shale gas deposits.

In addition to problems with experimental data, there is the question of choosing adequate adsorption models. For alkanes up to C_4H_{10}, as well as for CO_2 and some other non-hydrocarbon components, the monolayer Langmuir adsorption model (Langmuir, 1918) was found to be satisfactory in most studies:

$$n = n_{max}(T)\frac{b(T)\cdot P}{1+b(T)\cdot P},\qquad(8)$$

where n_{max} is the maximum amount of the substance (adsorbate) that can be adsorbed at given temperature T on the surface of the adsorbent; b is the adsorption equilibrium constant.

Higher alkanes require more complex models, such as the Toth model (Toth, 1971) and its modifications, or the BET model (Brunauer et al., 1938). Some examples of the application of these models for the adsorption of hydrocarbons are given in (Dong et al., 2016).

For multicomponent adsorption, the Langmuir model can be expanded by introducing fugacities instead of partial pressures, which leads to the following expression for the adsorption isotherm of an individual component of the mixture:

$$n_i = n_{max,i}\frac{b_i(T)f_i(P,T)}{1+\sum_{i=1}^{N} b_i(T)f_i(P,T)}.\qquad(9)$$

It is assumed that $n_{max,i}$ and b_i can be obtained using standard Langmuir analysis of experimental data on single-component adsorption.

Although the multi-component Langmuir model (MLM) (9) for alkanes up to C_4H_{10} gives satisfactory results in predicting the total amount of adsorbed mixture, it does not always adequately describe the adsorption selectivity, i.e. the adsorbed amount of each component. More complex models of multicomponent adsorption of hydrocarbons are presented and studied in the literature (Gusev et al., 1996), but none of them has been recognized as universally suitable for predicting adsorption at high pressures typical for oil and gas reservoirs (Sandoval et al., 2016).

Like the authors of (Sandoval et al., 2018), for the purposes of this work we limit ourselves to using the MLM model. Along with the reasons mentioned above, this choice is related to the input data of a shale reservoir adopted for test calculations, which we describe below. Nevertheless, it is important to emphasize that the proposed method allows the use of any model of multicomponent adsorption, which is of special importance for hydrocarbons higher than C_4H_{10} at pressures and temperatures typical for real reservoirs.

The choice of input data for following calculations was dictated, as mentioned, by practical absence of suitable experimental data for modelling of multicomponent adsorption of hydrocarbons at high pressures. As can be seen from the review in (Dong et al., 2016), there are no experimental data in the literature obtained at least for alkanes from methane to butane on the same adsorbent, at the same temperature and in a suitable pressure range. In the following examples, we use the data of (Ambrose et al., 2011) on the parameters of the Langmuir adsorption isotherms for hydrocarbons from methane to butane on shale rock at a temperature of 355°K (180°F) and pressures up to 310 bar (4500 psi) (Table 1). It should be noted that the data for butane in the (Ambrose et al., 2011) are obtained based on correlations of adsorption parameters with the number of carbon atoms in the alkane molecule.

Using the model of multi-component adsorption, one can calculate the adsorbed amount of each component. However, this is not enough to determine the composition of the adsorbed and free parts of the mixture in a porous medium for the following reasons.

• Although the adsorption process is associated with the pore surface, experimental data are usually available

Parameter	C1	C2	C3	C4
n_{max}, mmol/g	0.0670	0.109	0.214	0.277
b, 1/bar	0.009285	0.0179	0.0172	0.0409

Table 1. Langmuir coefficients for adsorption of pure alkanes on shale rock at 355 °K (according to (Ambrose et al., 2011), 1 bar = 10^5 Pa)

per unit mass of the adsorbent. This means that they cannot be transferred to adsorbents (reservoir zones) with different porosity, specific surface area of pores, mineral composition, content of bound water, etc., while in reality these characteristics are changed significantly even within the same deposit.

• The fraction of the adsorbed part of the mixture is a relative value. It depends not only on the adsorbed amount of mixture, but also on the total amount of the mixture per unit volume of pores (or specific surface area of pores) of the reservoir, which also varies significantly in actual conditions.

To overcome these two problems, we introduce into the model a single control parameter υ, which is expressed in mmol/g and corresponds to the total amount of the mixture per unit mass of the adsorbent (reservoir rock). Total amount of the mixture included in υ corresponds to hydrocarbons both in the adsorbed and free state.

The parameter υ can be treated as the total amount of hydrocarbons which "came" into the pores of a separate reservoir element, after which some part of it was adsorbed on the rock surface at current thermobaric conditions. Experimentally υ can be determined by extraction of all hydrocarbons from isolated rock element (sealed core specimen) of the reservoir. To account for reservoir heterogeneity, direct petrophysical dependencies of υ on reservoir parameters determined from well logs can be established and used. Note that to get the value of υ, one doesn't need to know free and adsorbed amounts of the mixture separately.

For an isolated reservoir element, value of υ remains constant under changes of pressure and temperature, while fractions, densities and other characteristics of the adsorbed and free parts of the mixture, as well as the number and properties of free (bulk) phases and even pore volume would change. Treating υ as constant is appropriate in the same bounds as total mixture composition $z_{bulk,i}$ in conventional PVT calculations. If simulated process assumes mass transfer between the element and the environment (e.g., constant volume depletion (CVD) or compositional simulation of fluid flow), then changes in υ are computed simultaneously with changes in $z_{bulk,i}$ by the balance of inflow/outflow to/from the reservoir element for each mixture component.

With a lack of direct experimental data, υ can be determined using information on the fraction of adsorbed hydrocarbons for a particular section of the reservoir or reservoir type at initial reservoir pressure p_0 and temperature T. For example, for the Barnett shale formation (USA), this fraction varies from 20 to 40 %. Given a certain value of the adsorbed fraction of hydrocarbons, initial approximation for υ can be calculated by determining the adsorbed amount of mixture at p_0 and T in a unit reservoir element from

the Langmuir equation (8) applied to the component with the largest concentration in the mixture. Then, phase equilibrium calculations are performed with multicomponent adsorption at p_0, T and given total mixture composition, as described in the next subsection. The total fraction of adsorbed hydrocarbons obtained using the model is compared with the actual one, and υ is adjusted accordingly. It may take several iterations. As soon as υ is adjusted by actual data, the model is ready for dynamic calculations, for example, with varying pressure.

Computational procedure

Since we consider the equilibrium phase behavior and adsorption, simulation of the process with dynamic changes in pressure (or/and temperature) can be performed in a sequence of independent calculations for each step in p (and T), as in conventional PVT simulations. The computational procedure for a given pressure and temperature is as follows.

An iterative loop is implemented. At each iteration, the phase equilibrium (flash) problem (5) is solved first for the total composition of the free part of the mixture z_i. Then, using the obtained fugacity values, the adsorbed amounts of each component n_{adsi} are determined with the multicomponent adsorption model (for example, the MLM model (9)). After that, the composition of the free part of the mixture is adjusted as follows:

$$z_i = \left(\upsilon \cdot z_{bulk,i} - n_{ads,i}\right)/\left(\upsilon - \sum_{j=1}^{N} n_{ads,j}\right),$$
$$i = 1,..,N, \tag{10}$$

or equivalently

$$z_i = \left(z_{bulk,i} - n_{ads,i}/\upsilon\right)/\left(1 - \sum_{j=1}^{N} n_{ads,j}/\upsilon\right),$$
$$i = 1,..,N, \tag{11}$$

where $z_{bulk,i}$ corresponds to the full total composition of the mixture (free + adsorbed part), and $z_i = z_{bulk,i}$ at the initial iteration.

A flowchart of the computational procedure in the case of calculating phase equilibria by the method of successive substitutions is shown in Fig. 1. According to the experience of the performed calculations, no more than 3-5 external iterations are usually required to find a solution (q-iterations in Fig. 1).

The following feature of the method is meaningful for practical applications.

The adsorbed amount of hydrocarbons in a reservoir element is determined by the fluid composition, pressure, temperature, and rock properties. Since reservoir rocks are highly inhomogeneous, application of, e.g., the method of (Sandoval et al., 2018) requires obtaining enough experimental data on multicomponent adsorption isotherms for different combinations of reservoir parameters – mineral composition, specific pore surface, pore size distribution, water content, etc., which is practically almost impossible.
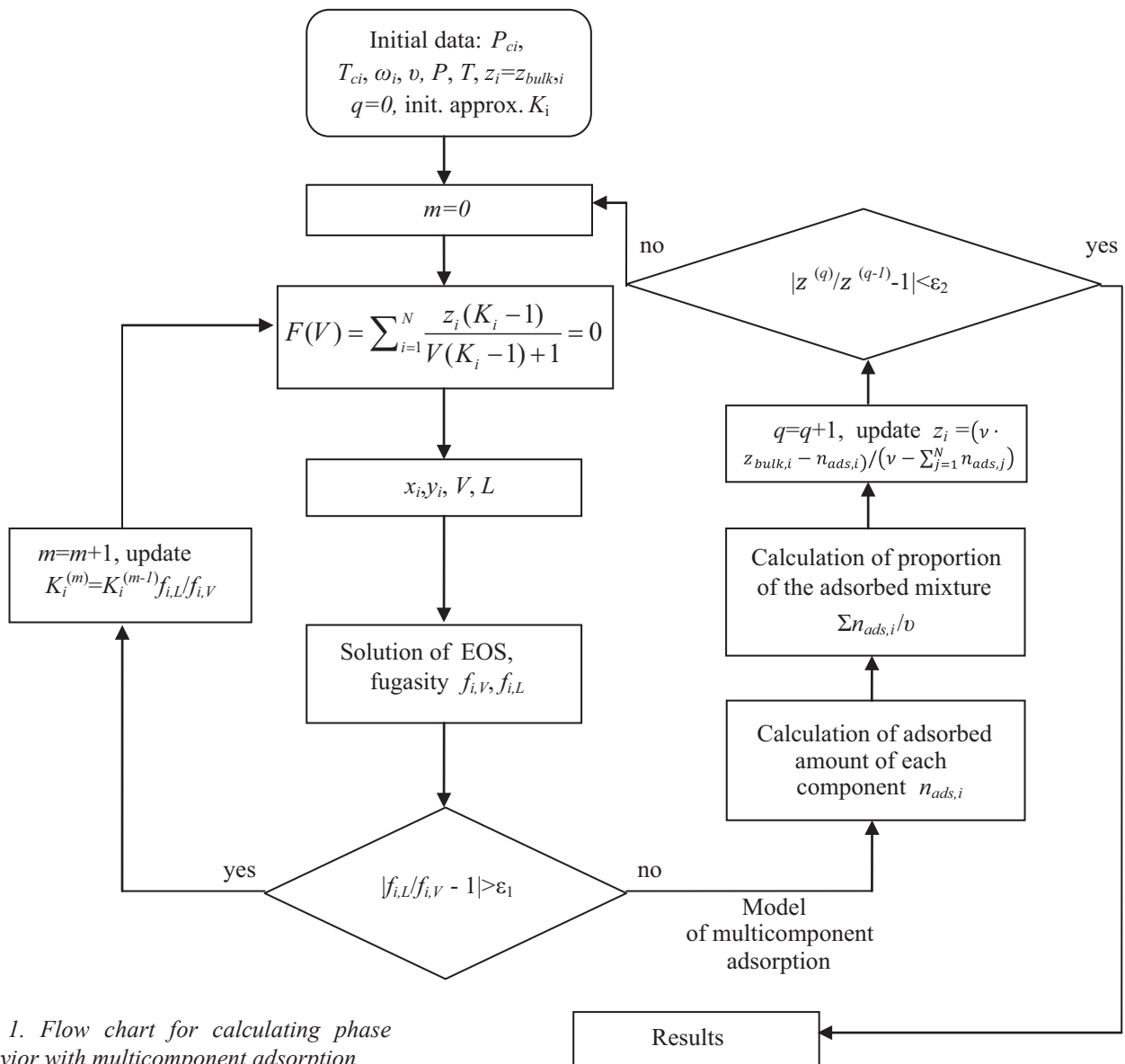
Fig. 1. Flow chart for calculating phase behavior with multicomponent adsorption

Within the framework of our method, in a lack of input data, the following approach can be used. Adjustment of v allows to "scale" multicomponent adsorption isotherms obtained in a limited number of experiments (or taken from similar rocks), so that the shape of the isotherm and relative adsorption of components (selectivity) are maintained, while the total adsorption intensity is matched according to variations in rock mineral composition and properties.

Specifically, for fixed thermobaric conditions and given parameters of the adsorption model, change in v would not influence the values of n_{adsi}. But as formula (11) shows, the effect of changing v on relative parameters – fraction of the free part of the mixture and its composition z_i – is equivalent to the effect of proportional change in n_{adsi}, i.e. "scaling" of adsorption isotherms. Thus, adjusting v (e.g., by matching initial fraction of the adsorbed mixture, as described above) allows to perform phase behavior calculations with account for adsorption in a lack of experimental data.

Example calculations

To illustrate the features of the model and evaluate the effect of dynamic adsorption/desorption on phase behavior, test calculations were performed for a three-component methane-ethane-butane mixture. The total mixture composition and thermobaric conditions are given in Table 2. Three cases with different values of v, also presented in Table 2, are considered. These values correspond to specified fractions of the adsorbed part of the mixture at initial pressure – 10, 25, or 40 %. The

Parameter	Value		
Total composition $z_{bulk,i}$, mol.%	C1 – 25, C2 –15, C4 – 60		
Temperature , °K	355		
Initial pressure, bar	276		
v, mmol/g	0.99	0.39	0.238
Initial fraction of adsorbed part of the mixture, mol.%	10	25	40

Table 2. Data for test calculations

parameters for the multicomponent MLM adsorption model are listed in Table 1.

The process of isothermal pressure depletion is simulated while maintaining the total composition of the mixture. In conventional PVT simulations, this corresponds to the process of constant composition expansion (CCE). However, in our case, the phase behavior cannot be described using the traditional calculation of CCE due to the dynamic changes in the composition of free part of the mixture.

Fig. 2 shows the free and adsorbed fractions of the components of the mixture at initial conditions ($p = 276$ bar) for the three cases with different v. All values are normalized by the total amount of the mixture. Note that due to the most intense adsorption of butane, its adsorbed fraction is larger than the adsorbed fraction of the mixture as a whole, whereas the opposite situation is observed for other components. The composition of free part of the mixture corresponds to the single-phase liquid state.

At $p = 100$ bar, the free part of the mixture remains single phase, but its composition is slightly different from the initial one due to the different relative desorption of the components. Table 3 shows how the total composition of the free part of the mixture changes with a decrease in pressure for $v = 0.238$ mmol/g.

For the accepted total composition of the mixture, the saturation pressure in bulk (no adsorption) is estimated at 68 bar. When calculated with adsorption for the free

Pressure, bar	Composition of the free part of the mixture z_i, mol. %		
	C1	C2	C4
276	0.2845	0.1652	0.5503
100	0.2949	0.1643	0.5408
70	0.2942	0.1635	0.5423
40	0.3397	0.1807	0.4797

Table 3. Composition of the free part of the mixture at various pressures and $v = 0,238$ mmol/g

part of the mixture, it increases by up to 5 bar (Table 4).

Fig. 3 shows the dynamics of the mole fraction of the vapor phase V versus pressure. Desorption of components leads to quite significant changes in phase behavior. For example, at $p = 50$ bar in bulk (without adsorption) the mole fraction of the vapor phase is $V = 0.38$, and for $v = 0.238$ mmol/g – $V = 0.56$.

In Fig. 3 the dotted line is of the greatest interest. It corresponds to the dynamics of the vapor phase fraction calculated using standard (in bulk) phase equilibrium algorithms. But here the mixture composition is taken to be equal to the composition of the free part of the mixture obtained at the initial pressure for the case $v = 0.238$ mmol/g. This corresponds to the situation when a sample of reservoir fluid is collected under initial reservoir conditions, and conventional PVT experiments and simulations are carried out on it. Despite the fact that the saturation pressure in this case turns out to be the same as when taking into account dynamic desorption, the dynamics of the phase behavior in the two-phase region are significantly different, and the fraction of the vapor phase is greatly underestimated. This clearly demonstrates the effect of dynamic adsorption/desorption on phase behavior, in contrast to static adsorption which affects only the initial composition of the mixture.
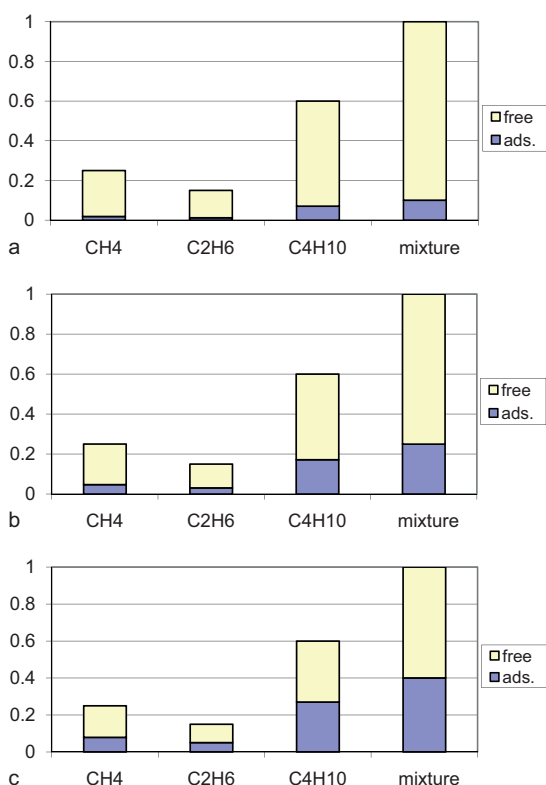

Fig. 2. Free and adsorbed fractions of the mixture components at initial pressure of 276 bar: a – $v = 0.99$, b – $v = 0.39$, c – $v = 0.238$ mmol/g

No adsorption	v, mmol/g		
	0.99	0.39	0.238
68	69	71	73

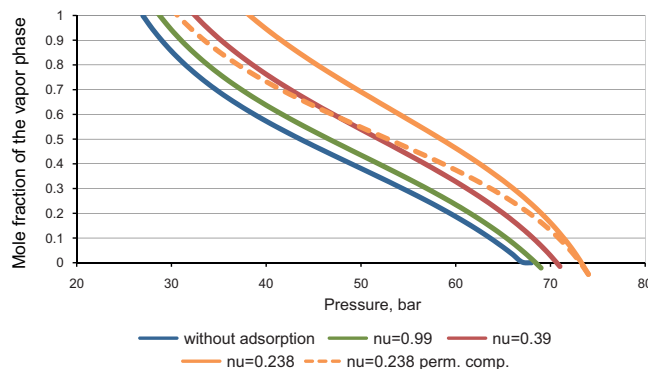*Table 4. Calculated saturation pressure, bar*

Fig. 3. Dynamics of the mole fraction of the vapor phase versus pressure at various values of v, mmol/g

It should also be noted that the most pronounced effect of different relative dynamics of the desorption of components is observed in the two-phase region (Table 3, Fig. 3). Fig. 4a and 4b show the dynamics of the mole fraction of methane and butane in the free part of the mixture for different values of v to illustrate this effect. Fig. 5 and 6 show the adsorbed and free fraction of each component in the vapor and liquid phases for two
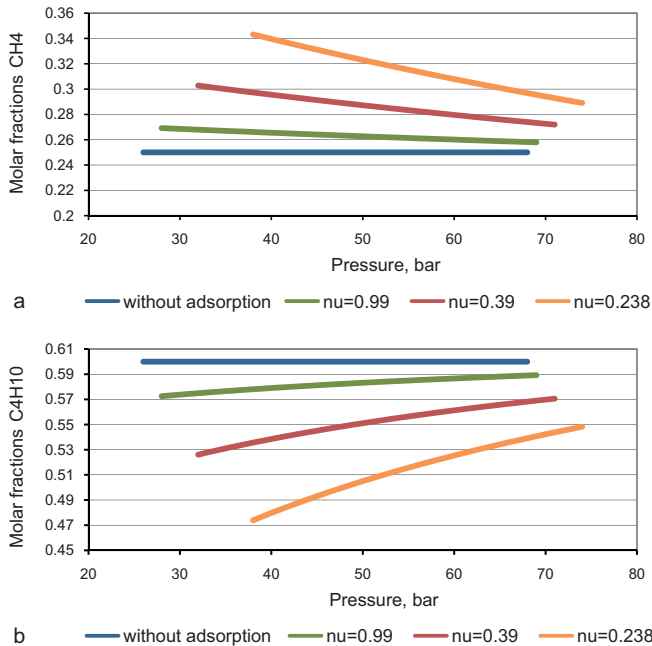

a

b

Fig. 4. Molar fractions of methane (a) and butane (b) versus pressure at various values of v, mmol/g

a

b

c
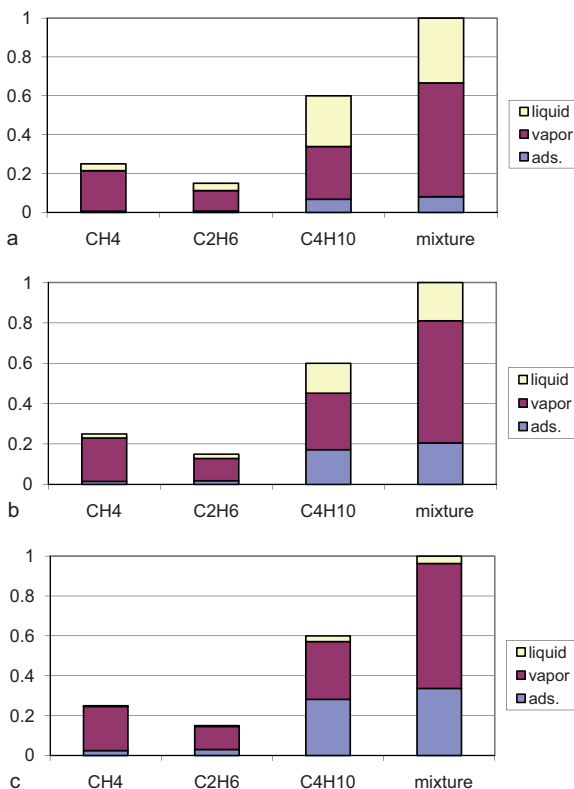
Fig. 5. Fractions of the mixture components in the adsorbed part, vapor and liquid phases at P = 65 bar: a – v = 0.99, b – v = 0.39, c – v = 0.238 mmol/g

a

b

c

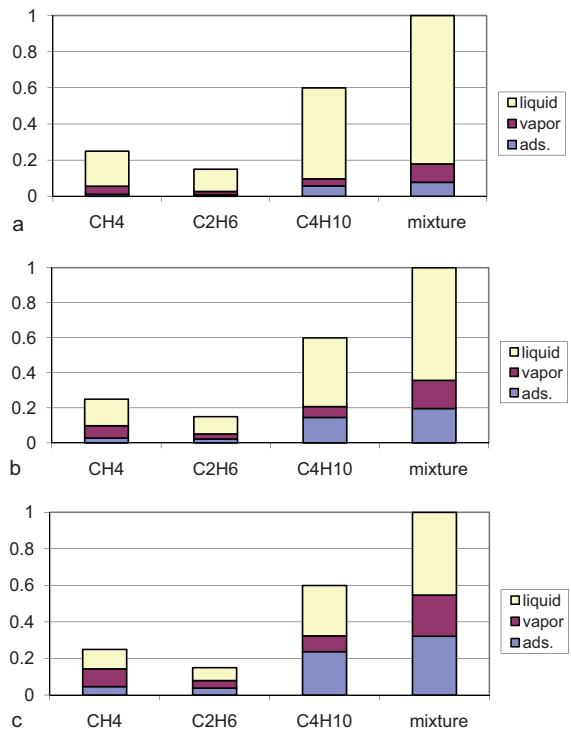*Fig. 6. Fractions of the mixture components in the adsorbed part, vapor and liquid phases at P = 40 bar: a – v = 0.99, b – v = 0.39, c – v = 0.238 mmol/g*

values of pressure in the two-phase region. Here again, the significant effect of multicomponent adsorption on the equilibrium fractions and compositions of the phases is evident.

Conclusions

In the paper, we presented a new method for phase behavior simulation of hydrocarbon mixtures under adsorption conditions. Dynamic multicomponent adsorption/desorption is considered as a key factor affecting the composition of the free part of the mixture and phase equilibrium. For calculations of the phase behavior in the presence of multicomponent adsorption, we presented a mathematical model, developed a computational algorithm and proposed a control parameter that takes into account variations in properties of the reservoir and the total adsorption intensity.

Test calculations were carried out for a three-component hydrocarbon mixture with adsorption and thermobaric parameters corresponding to the example of a real shale reservoir. The simulation results clearly demonstrate the significant effect of dynamic multicomponent adsorption/ desorption on phase behavior.

The mechanism described in the model can be critical in shale and tight reservoirs where a decrease in pressure leads to different relative desorption of components. This significantly affects the composition of the free part of the mixture, as well as the fracttions and compositions of the phases in the two-phase region. Therefore, the effect of multicomponent adsorption is to be considered dynamically.

References

Ambrose R.J., Hartman R.C., Labs W., Akkutlu I.Y. (2011). SPE 141416. Multi-component Sorbed-phase Considerations for Shale Gas-in-place Calculations. *SPE Production and Operations Symp.*, pp. 1-10. https://doi.org/10.2118/141416-MS

Aziz K., Wong T. (1989). Considerations in the development of multipurpose reservoir simulation models. *First and Second Forum on Reservoir Simulation*, pp. 77-208.

Brunauer S., Emmett P.H., Teller E. (1938). Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60(2), pp. 309-319. https://doi.org/10.1021/ja01269a023

Brusilovskii A.I. (2002). Phase transformations in the development of oil and gas fields. Moscow: Graal, 575 p.

Buleiko V.M., Voronov V.P., Zakirov S.N., Zakirov E.S., Indrupskii I.M. (2007). Regularities in the behavior of hydrocarbon systems of oil and gas pools. *Doklady Earth Sciences*, 415(1), pp. 686-689. https://doi.org/10.1134/S1028334X07050054

Choi B.U., Choi D.K., Lee Y.W., Lee B.K. (2003). Adsorption Equilibria of Methane, Ethane, Ethylene, Nitrogen, and Hydrogen onto Activated Carbon. *J. Chem. Eng.*, 48, pp. 603-607. https://doi.org/10.1021/je020161d

Coats K.H. (1998). Implicit Compositional Simulation of Single-Porosity and Dual-Porosity Reservoirs. *SPE Symp. on Reservoir Simulation*, SPE 18427

Dong X., Liu H., Hou J., Wu K. Chen Z. (2016). Phase Equilibria of Confined Fluids in Nanopores of Tight and Shale Rocks Considering the Effect of Capillary Pressure and Adsorption Film. *Industrial & Engineering Chemistry Research*, 55(3), pp. 798-811. https://doi.org/10.1021/acs.iecr.5b04276

Gusev V., O'Brien J.A., Jensen C.R.C., Seaton N.A. (1996). Theory for Multicomponent Adsorption Equilibrium: Multispace Adsorption Model. *AIChE Journal*, 42(10), pp. 2773-2783. https://doi.org/10.1002/aic.690421009

Jhavery B.S., Youngren G.K. (1988). Three-Parameter Modification of the Peng-Robinson Equation of State to Improve Volumetric Predictions. *SPE Reservoir Engineering*, 3, p. 1033. https://doi.org/10.2118/13118-PA

Langmuir I. (1918). The Adsorption of Gases on Plane Surface of Glass, Mica and Platinum. *The Research Laboratory of the General Electric Company*, 40, pp. 1361-1402. https://doi.org/10.1021/ja02242a004

Luo X., Wang S., Wang Z., Jing Z., Le M., Zhai Z., Han T. (2015). Adsorption of Methane, Carbon Dioxide and Their Binary Mixtures on Jurassic Shale from the Qaidam Basin in China. *Int. J. Coal Geol.*, 150-151, pp. 210-223. https://doi.org/10.1016/j.coal.2015.09.004

Matsumoto A., Zhao J., Tsutsumi K. (1997). Adsorption Behavior of Hydrocarbons on Slit-Shaped Micropores. *Langmuir*, 13, pp. 496-501. https://doi.org/10.1021/la950958l

Michelsen M.L. (1982a). The Isothermal Flash Problem. Part II. Phase-Split Calculation. *Fluid Phase Equilibria*, 9, pp. 21-40. https://doi.org/10.1016/0378-3812(82)85002-4

Michelsen M.L. (1982b). The Isothermal Flash Problem. Part I. Stability. *Fluid Phase Equilibria*, 9, pp. 1-19. https://doi.org/10.1016/0378-3812(82)85001-2

Nojabaei B., Johns R.T., Chu L. (2013). Effect of Capillary Pressure on Phase Behavior in Tight Rocks and Shales. *SPE Reservoir Eval. Eng.*, 16, pp. 281-289. https://doi.org/10.2118/159258-PA

Pang J., Zuo J., Zhang D., Du L. (2013). Effect of Porous Media on Saturation Pressure of Shale Gas and Shale Oil. *Proc. Int. Petro. Techn. Conf.* Beijing, pp. 1-7, IPTC 16419. https://doi.org/10.2523/IPTC-16419-MS

Pedersen K.S., Christensen P.L. (2006). Phase Behavior of Petroleum Reservoir Fluids. Taylor & Francis, USA. https://doi.org/10.1201/9781420018257

Peng D.Y., Robinson D.B. (1976). A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.*, 15, p. 59. https://doi.org/10.1021/i160057a011

Shapiro A., Stenby E.H. (2001). Thermodynamics of the Multicomponent Vapor-Liquid Equilibrium under Capillary Pressure Difference. *Fluid Phase Equilib.*, 178, pp. 17-32. https://doi.org/10.1016/S0378-3812(00)00403-9

Sandoval D., Yan W., Michelsen M., Stenby E. (2016). Model Comparison for High-pressure Adsorption in Shale and its Influence on Phase Equilibria. *ECMOR XV – 15th European Conference on the Mathematics of Oil Recovery*, Proc., Mo Efe 02. https://doi.org/10.3997/2214-4609.201601740

Sandoval D.R., Yan W., Michelsen M.L., Stenby E.H. (2018). Influence of Adsorption and Capillary Pressure on Phase Equilibria Inside Shale Reservoirs. *Energy & Fuels,* 32(3), pp. 2819-2833. https://doi.org/10.1021/acs.energyfuels.7b03274

Song L., Sun Z., Duan L., Gui J., McDougall G.S. (2007). Adsorption and Diffusion Properties of Hydrocarbons in Zeolites. *Microporous and Mesoporous Materials*, 104, pp. 115-128. https://doi.org/10.1016/j.micromeso.2007.01.015

Toth J. (1971). State Equations of the Solid Gas Interface Layer. *Act. Chim. Acad. Sci. Hung.*, 69, p. 311.

Wang Y., Tsotsis T.T., Jessen K. (2015). Competitive Sorption of Methane/Ethane Mixtures on Shale: Measurements and Modeling. *Ind. Eng. Chem. Res.,* 54, pp. 12187-12195. https://doi.org/10.1021/acs.iecr.5b02850

Whitson C.H., Brule M.R. (2000). Phase Behavior. SPE Monograph (Henry L. Doherty) Series, Vol. 20, SPE, Richardson, Texas USA.

Yun J.H., Duren T., Keil F.J., Seaton N.A. (2002). Adsorption of Methane, Ethane and Their Binary Mixtures on MCM-41: Experimental Evaluation of Methods for the Prediction of Adsorption Equilibrium. *Langmuir*, 18, pp. 2693-2701. https://doi.org/10.1021/la0155855

Zendehboudi S., Bahadori A. (2015). Shale Oil and Gas Handbook: Theory, Technologies, and Challenges. Gulf Professional Publ.

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