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OSCILLATORY MODES OF ADSORPTION IN THE SEEPAGE OF MULTICOMPONENT SYSTEMS†

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A system of equations describing the motion of multicomponent mixtures in a porous medium, taking into account the phenomena of competing adsorption is formulated within the framework of a kinetic approach to the study of sorption processes. An equation of sorption kinetics, which describes a series of oscillatory modes for certain values of the original parameters, is suggested. A numerical analysis of the stability is carried out for the corresponding dynamical system. A qualitative comparison of the results of calculations and experimental data is given. © 2003 Elsevier Science Ltd. All rights reserved.

Experimental investigations of absorption phenomena in multicomponent systems show the presence of competing effects, which lead to a non-monotonic distribution of adsorbents on the surface of a solid, where mutual influence of the components on the degree of adsorption of each of them is observed [1]. These effects are particularly important for flows of heavy oils containing surface-active components (asphaltenes, tars and naphthenic acids). The development of a theory of non-linear non-equilibrium dynamics of the adsorption of multicomponent mixtures is of theoretical and applied interest, due to adsorption separation of gaseous and liquid mixtures, the chromatographic effect in the seepage of oils, the displacement of petroleum by active admixtures and solvents, the injection of deposition inhibitors in oil wells, etc. [1–3]. On the other hand, a class of problems exists, connected with the manifestation of non-equilibrium phenomena in porous media. This is the seepage of fluids with complex rheological properties (liquid mud, non-Newtonian oils and polymers) and also two-phase seepage with a spatial redistribution of the phases and a variable phase permeability [4–6].

The purpose of this paper is to construct a theoretical model of competing adsorption in multi-component seepage flows, taking into account existing experimental data and modern ideas on the nature of non-equilibrium processes in porous media.

1. FORMULATION OF THE PROBLEM

The seepage of a multicomponent hydrocarbon system, including n surface-active components, diffusing in the porous space of a medium and simultaneously adsorbing on its surface is considered.

The dynamics of adsorption from a multicomponent mixture, moving in a porous medium, is described, in a one-dimensional diffusion model, by the equation of material balance of the ith component in pores and has the form

$$m\frac{\partial c_i}{\partial t} + \upsilon\frac{\partial c_i}{\partial x} + \frac{\partial a_i}{\partial t} = \frac{\partial}{\partial x}\left(D_i\frac{\partial c_i}{\partial x}\right), \quad 0 < x < L, \quad t > 0 \tag{1.1}$$

Here c_i is the concentration of the ith component in a moving phase, a_i is its concentration in the adsorbed state, υ is the average seepage rate of the mixture, m is the porosity, χ_j is the porosity, L are the characteristic dimensions of the porous medium, $D_i = D_{0i} + \chi_i\upsilon$ is the effective diffusion coefficient, and χ_j is the scattering parameter of the porous medium.

The sorption kinetics equations, which vary depending on the chosen adsorption model, must be added to system (1.1). Assuming that the main mass transfer occurs due to diffusion in the volume of the pores, we will consider the following kinetic equation for the adsorption model [7]

$$\partial a_i/\partial t = \beta_i c_i - F_i(a_1, \ldots, a_n)a_i \tag{1.2}$$

in which the function $F_i(a_1, \ldots, a_n)$, in the most general form, is written as follows:

$$F_1(a_1, \ldots, a_n) = b_i a_i \left(1 - \sum_i \lambda_i a_i \right)^{-p} - \sum_j k_{ij} a_j \qquad (1.3)$$

Here b_i is the adsorption coefficient of the ith component, λ_i is a coefficient, characterizing the degree of monolayer fillability, p is the assumed number of adsorption layers, and k_{ij} is the coefficient of intermolecular interaction of adsorbent components.

Equation (1.3) in the special case $n = 2$, $k_{ij} = 0$, $\lambda_i = 1$, $p = 1$ reflects Langmuir's adsorption theory for a two-component mixture [8]. If we take $n = 2$, $b_i = 0$, $k_{ij} \neq 0$, we obtain the classical system of Lotka–Volterra equations [9].

We will introduce the assumption of the possible non-equilibrium nature of the adsorption process due to the finite rate of the mass transfer at the surface of the skeleton of the porous medium and the characteristic delay time in establishing local thermodynamic equilibrium (at each point in space). In this case Eqs (1.1)–(1.3) must be supplemented with the relaxation equation

$$\tau \partial a_i / \partial t + a_i = \bar{a}_i \qquad (1.4)$$

Hence the solution with respect to the concentration of adsorbed substance, obtained from Eqs (1.1)–(1.3), is considered as the non-equilibrium value $\bar{a}_i$, and the required equilibrium value a_i is obtained more accurately from the solution of relaxation equation (1.4). The seepage rate in Eq. (1.1) is given by Darcy's law and the pressure distribution is obtained from the piezoconductivity equation. We get

$$\upsilon = -\frac{k}{\mu} \frac{\partial p}{\partial x}, \quad \frac{\partial p}{\partial t} = \frac{\partial}{\partial x} \left(\frac{k}{\mu m \beta} \frac{\partial p}{\partial x} \right), \quad \ln \mu = \sum_i c_i \ln \mu_i \qquad (1.5)$$

Here μ, β are the coefficients of dynamic viscosity and the compressibility of the seepage mixture, respectively and k is the permeability of the saturated porous medium; the viscosity of the mixture depends on the coefficients of dynamic viscosity of the components μ_i and is given by the last relation of Eq. (1.5).

Equations (1.1)–(1.5) are supplemented by the following initial and boundary conditions

$$\begin{aligned}
c_i(0, t) &= c_i^0, \quad \partial c_i / \partial x|_{x=L} = 0, \quad t \geq 0, \quad 1 \leq i \leq n \\
a_i(x, 0) &= 0, \quad c_i(x, 0) = c_{0i}, \quad 0 < x < L \\
p(0, t) &= p_1, \quad p(x, 0) = p_0, \quad p(L, t) = p_0
\end{aligned} \qquad (1.6)$$

2. NUMERICAL ANALYSIS OF THE STABILITY OF THE DYNAMICAL SYSTEM

The solutions of the problem depend very much on the form of the function $F_i(a_1, \ldots, a_n)$ in Eq. (1.3), as has been shown by numerical experiments. The system considered exhibits unexpected behaviour, including oscillations in the solutions $a_i(x, t)$, which, in turn, can give rise several extrema in the solutions $c_i(x, t)$. In this connection, the stability of the system of equations of sorption kinetics (1.2), (1.3) was analysed for the case of two simultaneously adsorbing components

$$\frac{\partial a_i}{\partial t} = \beta_i c_i - \frac{b_i a_i^2}{(1 - \lambda_1 a_1 - \lambda_2 a_2)^2} + k_i a_1 a_2, \quad i = 1, 2 \qquad (2.1)$$

The stability of the equilibrium positions of system (2.1) at a fixed point in space ($x = 0$) was analysed numerically by the Runge–Kutta method for a wide range of values of its coefficients. All the results obtained can be divided into two classes: (1) solutions of the travelling concentration wave type, occurring in cases when one of the components clearly predominates over the others either in speed, or in degree of adsorption activity on the surface of the skeleton of the porous medium, and (2) solutions corresponding to the various oscillatory processes. Solutions of the second class are of the greatest interest
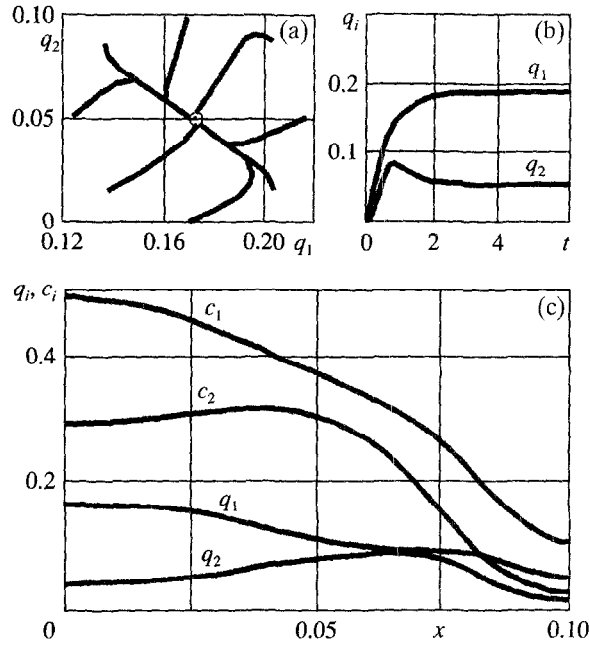
Fig. 1

from the point of view of confirming the competitive of the adsorption. Various types of oscillations are possible in the concentration distributions as was shown by the numerical experiment.

The calculations were carried out for fixed values of the following initial parameters

$$\beta_1 = 0.5, \quad \beta_2 = 0.4, \quad k_2 = 10, \quad \lambda_1 = \lambda_2 = 0.5, \quad c_1^0 = 0.5, \quad c_2^0 = 0.3$$

and for the following sets of values of the other parameters

$$k_1 = -30, \quad b_1 = 0.005, \quad b_2 = 0.1 \quad \text{(Fig. 1)}$$
$$k_1 = -50, \quad b_1 = -0.005, \quad b_2 = 0.5 \quad \text{(Fig. 2)}$$
$$k_1 = -30, \quad b_1 = -0.005, \quad b_2 = 0.1 \quad \text{(Fig. 3)}$$

The results are shown in Figs 1–3(a) in the form of phase diagrams in the (q_1, q_2) plane, where $q_i = a_i/c_i^0$ are the values of the concentration of the adsorbed component, referred to the maximum value (the limiting value at the point $x = 0$) of the concentration of the given component in the porous space. The graphs of $q_i(t)$ corresponding to the results obtained are given in Figs 1–3(b).

It is can be seen that an insignificant change in the values of some parameters substantially changes the nature of the process from decaying oscillations, which, as is well known, is due to the presence of a singular point of the *stable focus* type (Fig. 2a), to sustained self-excited oscillations, connected with the occurrence of singular points of the *unstable focus* type and limiting cycles (Fig. 3a) in the system. Fig. 1(a) (a *stable mode*) illustrates the case when there are no oscillations.

3. NUMERICAL SOLUTION OF THE BOUNDARY-VALUE PROBLEM

The initial-boundary-value problem (1.1)–(1.6) formulated above in the special case of two-component adsorption ($i = 1.2, C_i(x, 0) = 0$) was solved numerically by a difference method and using the checkerboard scheme for the following, values of the initial parameters, apart from those mentioned above.

$$m = 0.2, \quad k = 0.5 \times 10^{-12} \, \text{m}^2, \quad \mu_1 = 0.8 \, \text{Pa s}, \quad \mu_2 = 0.2 \, \text{Pa s}, \quad \mu_0 = 0.01 \, \text{Pa s}$$

$$\chi_1 = \chi_2 = 0.1 \, \text{m}, \quad \beta = 10^{-9} \, \text{Pa}^{-1}, \quad \tau = 0.02 \, \text{s}, \quad L = 100 \, \text{m},$$

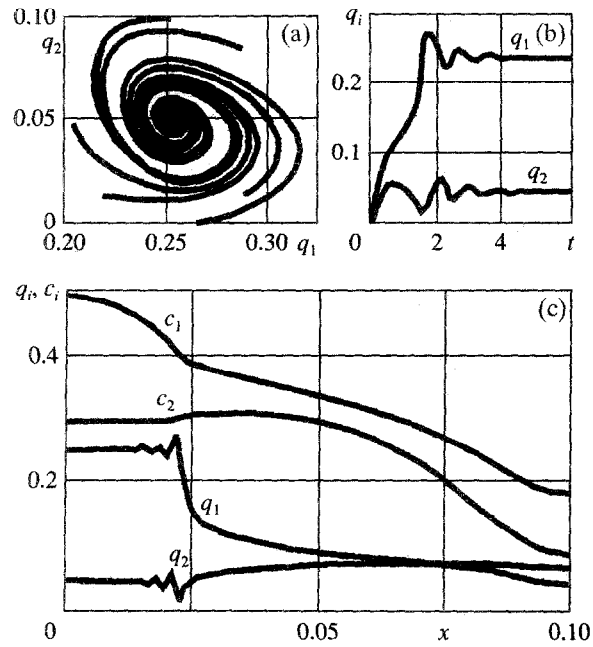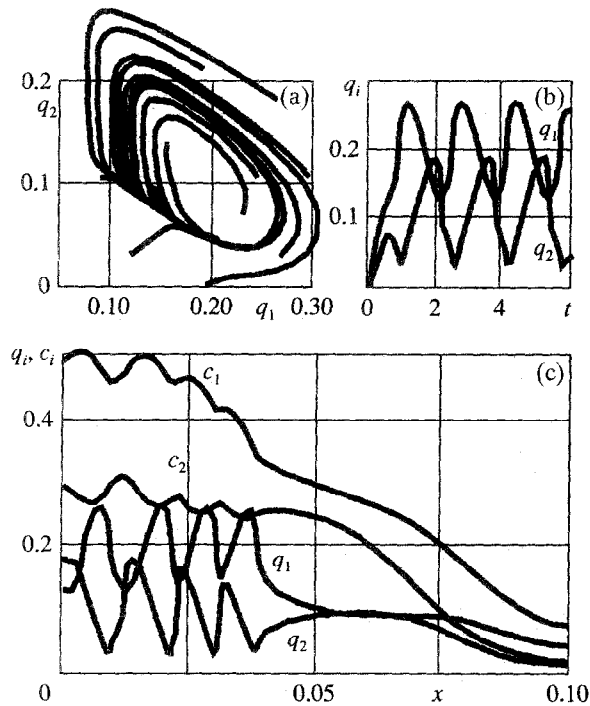$$p_0 = 10^7 \, \text{Pa}, \quad p_1 = 1.5 \times 10^7 \, \text{Pa}$$

Fig. 2

Fig. 3

It has been established that this system behaves quite differently, depending on the initial data and parameters. The concentration distributions in space, corresponding to the three qualitatively different cases considered at the boundary point $x = 0$, are shown in Figs 1–3(c). It can be seen that in both cases when oscillations (Figs 2 and 3) are observed in the dynamical system, the response to the oscillations excited at the boundary point occurs after certain time intervals (in the figures above – of the order of several hours). However, whereas in the first case (Fig. 2b) the oscillations occur only in the concentration distribution of the adsorbed substances, in the second case (Fig. 3b) they are so
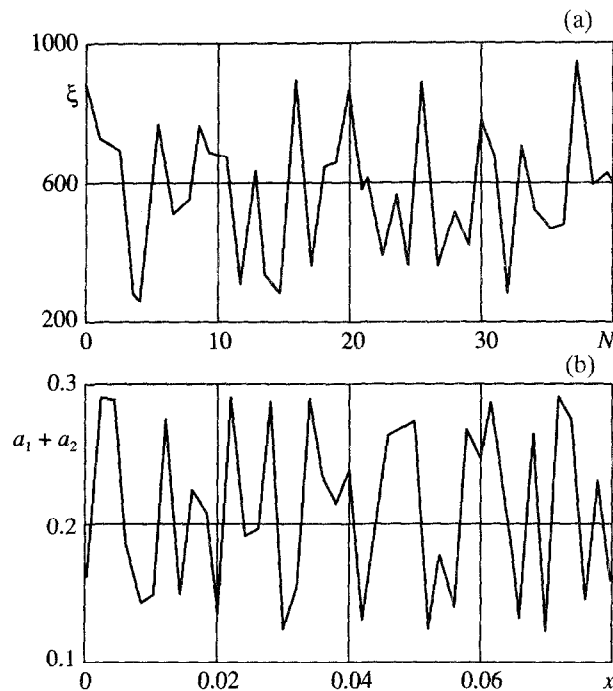
Fig. 4

pronounced, that, in their turn, they also generate oscillations of the concentrations of the components in the flow.

It can be seen from the figures that the existence of a travelling concentration front, moving in space with a gradual increase in the concentration up to a certain maximum value, is characteristic for each adsorbed substance. This front blurs out with time, since, simultaneously with the adsorption process, partial desorption of the component occurs, which is carried away by the fluid flow. The concentration distributions are oscillations of different forms for the chosen initial data. The adsorption of one component is initially suppressed by the other, but then the first component starts to occupy the adsorption centres more rapidly which also leads to an oscillatory mode, confirming the competing nature of the sorption process.

4. COMPARISON WITH EXPERIMENT

The conclusions on the behaviour of the parameters of multicomponent sorption, obtained on the basis of the mathematic model, agree completely with the results of specially conducted experiments [10]. Adsorption chromatographic effects, which occur during the seepage of the highly viscous oil from the Arlan oil field with a high content of surface-active components, were studied. PVC pipes with a length of 1 m and a diameter of 22 mm filled with quartz sand were used as models of porous media. In all the experiments, after the completion of the seepage process, the pipe was cut into 10, 20 or 40 elements, each of which was examined to estimate the degree of adsorption along the length of the model of the porous medium. The free, unadsorbed, part of the seeped fluid from each element was separated on a centrifuge and the remaining part was extracted using well-known methods and examined photocolorimetrically. The light absorption coefficient ξ, which quantitatively characterizes the content of the adsorbed residue [1, 2], was measured. The longitudinal distribution of ξ along the model of the porous medium was found to be non-linear. This is confirmed by the dependence of ξ for the model divided into 40 analysed elements, given in Fig. 4(a).

The initial-boundary-value problem (1.1)–(1.6) in the case of two components was solved under conditions that approximated as closely as possible the experimental ones in order to compare the results of the experimental and theoretical analysis. The results cannot pretend to be a quantitative comparison since the values of ξ only give an indirect representation of the content of adsorbed substances in the experiments, while approximate values of the coefficients are used in the theoretical formulation. A graph of the total concentration of the absorbed components as a function of the space coordinate at fixed points of space (which corresponds to the conditions of the experiment) is given in Fig. 4(b).

The results obtained show good qualitative similarity between the numerical calculations and the experimental data and the oscillatory nature of the competing adsorption processes.

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