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Competitive adsorption of a two-component gas on a deformable adsorbent

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Abstract

We investigate the competitive adsorption of a two-component gas on the surface of an adsorbent whose adsorption properties vary due to the adsorbent deformation. The essential difference of adsorption isotherms for a deformable adsorbent both from the classical Langmuir adsorption isotherms of a two-component gas and from the adsorption isotherms of a one-component gas is obtained, taking into account variations in the adsorption properties of the adsorbent in adsorption. We establish bistability and tristability of the system caused by variations in adsorption properties of the adsorbent in competitive adsorption of gas particles on it. We derive conditions under which adsorption isotherms of a binary gas mixture have two stable asymptotes. It is shown that the specific features of the behavior of the system under study can be described in terms of a potential of the known explicit form.

Keywords: adsorption, isotherm, bistability, adsorbent, hysteresis

(Some figures may appear in color only in the online journal)

Nomenclature

C_n	concentration of gas particles of species n
E_n^a, E_n^a	activation energies for adsorption and desorption,
$\mathbf{F}^{d}(\mathbf{x})$	respectively, of particles of species <i>n</i>
$E_n(x)$	activation energy for desorption of adparticles of
	species <i>n</i> from the surface of a deformable
	ausorbent
\vec{e}_x	unit vector along the $0X$ -axis
$\vec{F}_n(x,t)$	time-step adsorption-induced force acting on the
	adsorption site occupied by an adparticle of
	species n
$\vec{F}_n(x)$	adsorption-induced force acting on the
	adsorption site permanently occupied by an
	adparticle of species n
$\vec{F}(x,t)$	effective time-continuous adsorption-induced
	force acting on the adsorption site
G	ratio of the constant adsorption-induced forces
	acting on the adsorption site occupied by
	adparticles of species 2 and 1, respectively
g	coupling parameter in adsorption of a
	one-component gas or a two-component gas
	whose particles identically act on the adsorbent

gc .	critical value of g in adsorption of a
	one-component gas
g_n	coupling parameter of adparticles of species n
$I_+(g)$	width of the bistability interval in the case of
	adparticles identically acting on an adsorbent
$I_{n,m}$	widths of the (first, $n = 2, m = 1$), (second,
	n = 4, m = 3) and (single, $n = 2, m = 3$)
	bistability intervals
K_n	classical adsorption equilibrium constant for a
	one-component gas of species n
k_{n}^{+}, k_{n}^{-}	pre-exponential factors of the rate constants for
	adsorption and desorption k_n^a , k_n^d , respectively, of
	particles of species <i>n</i> in the classical case
$k_n^{\rm d}(x)$	rate coefficient for desorption of adparticles of
	species <i>n</i> from the surface of a deformable
	adsorbent
k _B	Boltzmann constant
ℓ_n	dimensionless concentration of gas particles of
	species n
$\ell^{b}_{1,k}$	the <i>k</i> th bifurcation value of ℓ_1 ; $k = 1, 2, 3, 4$
$\ell^{\mathrm{b}}_{d}, \ell^{\mathrm{b}}_{t}, \ell^{\mathrm{b}}_{u}$	bifurcation values of ℓ_1 giving two two-fold
u i u	solutions
ℓ_{1k}^{c}	the <i>k</i> th critical value of ℓ_1 ; $k = 1, 2, 3$;
-,	$(\ell_{1,+}^{c} \equiv \ell_{1,2}^{c}, \ell_{1,-}^{c} \equiv \ell_{1,3}^{c})$

1

$\ell_{1,1}^{t}, \ell_{1,2}^{t}$	boundary values of ℓ_1 of the tristability interval	Ì
ℓ_+	summary dimensionless concentration of gas	1
	particles	1
$\ell^{\mathrm{b}}_{+,k}$	the <i>k</i> th bifurcation value of ℓ_+ ; $k = 1, 2$	1
ℓ_{+}^{c}	critical value of ℓ_+	1
$\ell_+^{\rm M}$	Maxwell concentration	1
$\ell_1^{\text{but}}, S_0^{\text{but}},$		2
$g_1^{\text{but}}, G^{\text{but}}$	coordinates of a point in the four-dimensional	ı
	space of control parameters $\{\ell_1, S_0, g_1, G\}$	
	giving a five-fold three-component stationary	(
	solution $\xi^{\text{but}}, \theta_1^{\text{but}}, \theta_2^{\text{but}}$	
m_0, m_n	masses of a vacant adsorption site and a gas	C
	particle of species <i>n</i> , respectively	8
$m_{\rm eff}(\Theta)$	effective mass of oscillator	1
Ν	total number of adsorption sites	
N_n	number of adsorption sites occupied by	(
	adparticles of species <i>n</i>	ϵ
$N_{\rm b}, N_0$	numbers of occupied and vacant adsorption sites,	
	respectively	ϵ
$P_{+}, P_{-},$		ϵ
$P_1, P_d,$		
P_t, P_u, P_{but}	singular points of the bifurcation curve	ϵ
$R_0, R(\xi)$	ratios of the residence times of adparticles of	ϵ
	species 2 and 1 on the surface of nondeformable	e
→	and deformable adsorbents, respectively	ϵ
r	running coordinate of the adsorption site	e
S_0	ratio of the dimensionless concentrations of gas	e
~ ~ ~	particles of species 2 and 1	ϵ
S_t, S_d, S_u	values of S_0 giving two two-fold solutions	2
S_k^c	the <i>k</i> th critical value of S_0 ; $k = 1, 2, 3$;	ξ
cM	$(S_+^c \equiv S_2^c, S^c \equiv S_3^c)$	ξ
S_0^{M}	Maxwell value of S_0	
$S(\xi)$	ratio of the surface coverages by adparticles of	ξ
Т	species 2 and 1	ξ
1	absolute temperature	ξ
l LL(S)	time	\$
$U(\xi)$	potential in the adiabatic approximation $U(\xi)$ at ξ	ξ
U_k	value of the potential $U(\xi)$ at $\xi = \xi_k$;	۶
$IIa(\mathcal{E})$	k = 1, 2, 5, 4, 5	Ş
$U(\xi)$	potential $O(\xi)$ as $\ell_1 \to \infty$	e
$V_n(X)$	potential of the adsorption-induced force $F_n(x)$	\$
$-\mathbf{v}_n$	desorption of admarticles of species <i>n</i> coursed by	ξ
	the adsorbent deformation in adsorption of a	t
	one-component gas of species n	
11).	width of the interval of instability of A .	٤
w ₊ r	spatial variable in equations (58) (68) and (71)	5
$r^{eq}(\Theta)$	equilibrium position of the oscillator in	· ·
(0)	adsorption of a two-component gas	
$x_n^{eq}(\theta_n)$	equilibrium position of the oscillator in	7
···n (°n)	adsorption of a one-component gas of species n	<i>i</i>
x ^{max}	maximum displacement of the equilibrium	
n	position of oscillator in adsorption of a	
	one-component gas of species <i>n</i>	7
$G_n, g^a, h.$		
$I^{\mathrm{a}}_{\mathrm{I}}, I^{\mathrm{a}}_{\mathrm{I}}, M$		
q, q_a, S_a^a		1
S^{a}, S^{a}, S^{a} .		
U^{M} . $U^{\mathrm{a}}_{\mathrm{M}}$.		1
- , ~ M,		

quantities defined in the text

 w_{a}

 $\begin{array}{ll} D(\xi), h(\xi), \\ I_{a}(g_{1}, G) \\ L(\xi; g_{1}, G, S_{0}), \\ L_{1}(\xi; g_{1}), \\ L_{2}(\xi; g_{1}, G), \\ L_{c}(\xi; g_{1}, G), \\ S^{a}(g_{1}, G), \\ w(\xi) \end{array}$ functions defined in the text

Greek symbols

α	friction coefficient				
ε	arbitrary small positive value				
η	positive solution of one of the				
	equations: (58), (68) and (71)				
Θ	collection of the surface coverages θ_1 and θ_2				
θ^{L}	classical Langmuir surface coverage by				
° n	adparticles of species <i>n</i>				
θ	surface coverage by adparticles of species n				
$\theta^a \theta^a$.	single and kth asymptotic values of θ_{i}				
$o_n, o_{n,k}$	respectively; $k = 1, 2, 3$				
θ_{n}^{a} , θ_{n}^{a}	doubly degenerate asymptotic values of θ_n				
θ_c^{a}	triply degenerate asymptotic value of θ_n				
$\tilde{\theta_{+}}$	surface coverage by adparticles of both species				
$\theta_{\pm k}$	solutions of equation (36); $k = 1, 2, 3$				
$\theta^{b}_{b}_{b}$	the <i>k</i> th bifurcation value of θ_+ ; $k = 1, 2$				
θ_{c}^{c}	critical value of θ_{\pm}				
θ_0	vacant part of the adsorbent surface				
и И	restoring force constant				
<u>ج</u>	dimensionless coordinate of oscillator				
za za	single and kth asymptotic values of ξ				
אלי ל	respectively: $k = 1, 2, 3$				
za za	doubly degenerate asymptotic values of ξ				
5+,5- Ea	triply degenerate asymptotic value of ξ				
5 _с ⊱М ⊱М	values of ξ at which potential (67) with $\ell_{\perp} = \ell^{\rm M}$				
5+ ,2-	has equal minima				
Ea Ea	values of ξ at which the potential $U^{a}(\xi)$ with				
SM+, SM−	$S_{0} = S^{M}$ has equal minima				
εb дb	$S_0 = S_0$ has equal minima				
Δb	components of the kth two fold stationary				
$0_{2,k}$	components of the kill two-fold stationary solution: $k = 1, 2, 3, 4$				
5C DC	solution, $k = 1, 2, 3, 4$				
$\boldsymbol{\xi}_k, \boldsymbol{\theta}_{1,k},$	components of the <i>k</i> th three fold stationers				
$\theta_{2,k}$	components of the kulturee-fold stationary				
	solution; $k = 1, 2, 3; (\xi_{+}^{+} \equiv \xi_{2}^{-}, \xi_{-}^{-} \equiv \xi_{3}^{-};$				
Sa	$\theta_{n,+}^{*} \equiv \theta_{n,2}^{*}, \theta_{n,-}^{*} \equiv \theta_{n,3}^{*}$				
5k	roots of equation (18); $k = 1, 2, 3, 4, 5$				
τ_n^u	infetime of a vacant adsorption site in the				
	classical adsorption of a one-component gas of				
d dws	species n				
$\tau_n^{\mathrm{u}}, \tau_n^{\mathrm{u}}(\xi)$	classical and coordinate-dependent residence				
	times of adparticles of species <i>n</i> on the surface of				
	nondeformable and deformable adsorbents,				
ha	respectively				
$\tau_n^{\rm ad}$	time taken for the surface coverage θ_n to reach				
	the stationary value in the Langmuir adsorption				
	of a one-component gas of species n				
$ au_{ m r}$	relaxation time of a massless oscillator in the				
	linear case				
$ au_ heta$	relaxation time of $\theta_n(t)$ in the Langmuir				
	adsorption				

Xn	constant adsorption-induced force acting on the
	adsorption site occupied by an adparticle of
	species <i>n</i>
ω_M	vibration frequency of an oscillator of mass M
$\beta, \beta_+,$	
$\beta_{-}, \delta^{u},$	
$\delta_{n+1,n}, \theta_1^u,$	
$ au_M$	quantities defined in the text

1. Introduction

Problems of adsorption on the surface of different bodies belong to a wide class of problems of physics, chemistry and biology that are very important both from the theoretical point of view and for various practical applications. The results of numerous investigations show that adsorption of particles leads to considerable changes in the physical and chemical characteristics of adsorbents. A detailed analysis of the changes in the properties of the adsorbent surface due to adsorption is given, for example, in [1–11].

Since processes of adsorption and desorption are obligatory stages of heterogeneous catalytic reactions, the results of the adsorption theory are extremely important for investigation of various problems of heterogeneous catalysis [12-17].

Generalizations of the classical Langmuir adsorption theory aimed at a more correct description of the adsorbent surface and adparticles (adsorbed particles) give the qualitatively new behavior of the amount of adsorbed substance and its kinetics. Extensive material obtained on the basis of different models and applications to various problems of adsorption and catalysis are widely presented in the literature (see e.g. [8, 13-22]). In particular, due to lateral interactions between adparticles, adsorption isotherms can have a hysteresis shape, and different structural changes in the adsorbent surface occur (reviews of the theoretical and experimental results are given, for example, in [8-11, 19–22]). In turn, a qualitative change in the surface structure in adsorption leads to a series of specific features of oscillatory surface reactions and formation of different spatiotemporal patterns (for the oscillatory kinetics in heterogeneous catalysis and related problems, see for example the reviews [23-25] and the monograph [26]).

It is established in [27] that, parallel with lateral interactions between adparticles, there is another factor (the adsorption-induced deformation of an adsorbent) leading to hysteresis-shaped isotherms of localized adsorption of a one-component gas on the flat energetically homogeneous surface of a solid adsorbent. It is worth noting that, as early as 1938, based on the idea of a change in adsorption properties of the adsorbent surface in adsorption, Zeldovich [28] predicted a hysteresis of adsorption isotherms if the typical time of adsorption and desorption is much less than the relaxation time of the surface.

In recent years, it has been established that there is an essential influence of memory effects on the surface diffusion of adparticles over the adsorbent surface in the case where the relaxation time of the adsorbent is comparable with (or greater than) typical times for moving adparticles (see for example the review [29] and references therein). Dynamical changes in the properties of the surface by moving particles are taken into account in some models (e.g. in [30, 31]), which, to some extent, is similar to the Zeldovich idea of an absorbent varying its adsorption properties in adsorption.

Since an actual adsorbate has several species of particles, in adsorption, particles of different species compete for adsorption sites. This leads not only to a decrease in the number of adparticles of a species relative to that for one-component adsorption [19, 21, 22, 32, 33] but also to a qualitative change in the shape of adsorption isotherms with regard to lateral interactions between adparticles [20]. In view of hysteresis-shaped isotherms of localized adsorption of a one-component gas on the flat surface of a solid adsorbent due to the adsorption-induced deformation of an adsorbent [27], it is of interest to investigate the influence of this factor on changes in the classical extended Langmuir adsorption isotherms of a multicomponent gaseous system.

In the present paper, we study specific features of adsorption isotherms of a two-component gas on the surface of a solid adsorbent whose adsorption properties vary in adsorption.

In section 2, a model of adsorption of a two-component gas is proposed, taking into account variations in the adsorption properties of an adsorbent caused by its deformation in adsorption. We obtain a system of equations that describes the kinetics of the surface coverage and the displacement of adsorption sites. The influence of the adsorbent deformation on the adsorption isotherms is investigated in section 3. It is established that there is a considerable redistribution of the amount of adsorbed substances as compared with that in the classical case, even for a negligible quantity of particles of one species in a gas mixture. The obtained adsorption isotherms essentially depend on the introduced coupling parameters and differ both from the Langmuir adsorption isotherms of a two-component gas and from the adsorption isotherms of a one-component gas for an adsorbent whose adsorption properties vary in adsorption. We establish bistability and tristability of the system caused by variations in the adsorption properties of the adsorbent in competitive adsorption. Conditions under which adsorption isotherms of a binary gas mixture have two stable asymptotes are derived. In section 4, within the framework of the overdamped approximation and essential difference in the linear relaxation times of the dynamical variables, the behavior of the system under study is described in terms of a potential whose explicit form is obtained. The specific features of isotherms of competitive adsorption are explained with the use of the single-, two- or three-well potential.

2. General relations

We consider localized monolayer competitive adsorption of particles of a two-component gas on the flat surface of a solid adsorbent by using the classical Langmuir model generalized to the case of variations in adsorption properties of the adsorbent in adsorption/desorption of gas particles [27]. Gas particles are adsorbed on adsorption sites located at the adsorbent surface and the total number of sites N does not change with time. All adsorption sites have equal adsorption activity and each adsorption site can be bound with only one gas particle. We introduce the Cartesian coordinate system with the origin on the adsorbent surface and the 0X-axis directed into the adsorbent so that the adsorbent and the gas occupy the regions $x \ge 0$ and x < 0, respectively.

Following [27], we simulate each vacant adsorption site by a one-dimensional linear oscillator of mass m_0 that oscillates perpendicularly to the surface about its equilibrium position x = 0.

The binding of a gas particle with an adsorption site is accompanied by a change in the spatial distribution of the charge density of the bound adsorption site as compared with that of a vacant one. This change depends on the nature of adsorption bonds and specific features of both the adsorbent and gas particles (see e.g. [3, 8, 9, 23-26, 34]).

This leads to a change in the interaction of the bound adsorption site with neighboring atoms of the adsorbent located both on the surface and in the nearest subsurface region. As a result, the resulting force acting on the bound adsorption site changes compared to that acting on the vacant adsorption site. This can be regarded as the appearance of an adsorption-induced force $\vec{F}_n(\vec{r}, t)$ acting on the adsorption site occupied by an adparticle of species n = 1, 2 (here and below, the subscript n = 1, 2 denotes the species of particles), where \vec{r} is the running coordinate of the adsorption site. Under the action of this force, the bound adsorption site tends to a new equilibrium position. However, as soon as the adparticle leaves the adsorption site, the last site becomes vacant and relaxes to its nonperturbed equilibrium position x = 0. For the subsequent adsorption of other gas particles on this vacant adsorption site, two essentially different situations are possible: a gas particle occupies the site after or before it reaches the nonperturbed equilibrium position. In the first case, a new adparticle on the adsorption site does not 'fill' the space occupied by previous adparticles. In the second, a particle is adsorbed on the surface locally deformed by the previous adparticle (not necessarily of the same species), i.e. the retardation of relaxation of the surface occurs or, in other words, adsorption with memory takes place.

We consider the case where the force $\vec{F}_n(\vec{r}, t)$ is normal to the boundary and depends only on the coordinate *x*: $\vec{F}_n(\vec{r}, t) \equiv \vec{F}_n(x, t) = \vec{e}_x F_n(x, t)$, where \vec{e}_x is the unit vector along the 0*X*-axis.

The time-step force $\vec{F}_n(x, t)$ acts on the adsorption site only during discrete time intervals where the site is bound. Thus, at any instant, the adsorption site is in one of three states: vacant or bound with an adparticle of species 1 or 2. Instead, we consider the approximation of an effective time-continuous adsorption-induced force F(x, t)acting on the adsorption site that takes into account the presence of an adparticle on the adsorption site in the mean, i.e. the adsorption site is permanently bound with an adparticle but with the time-dependent probability (the mean occupancy of an adparticle on an adsorption site) equal to the surface coverage by adparticles of species $n, \theta_n =$ $N_n(t)/N$, where $N_n(t)$ is the number of adsorption sites occupied by adparticles of species n at the time t. Since an adsorption site can be bound only with one adparticle, $\dot{F}(x,t) = \dot{F}_1(x) \theta_1 + \dot{F}_2(x) \theta_2$, where $\dot{F}_n(x) = \vec{e}_x F_n(x)$ is the adsorption-induced force acting on the adsorption site permanently occupied by an adparticle of species n, and, hence, $\vec{F}(x,t) = \vec{e}_x F(x,t)$, $F(x,t) = F_1(x) \theta_1 + F_2(x) \theta_2$. This approximation is similar to the mean-field approximation used in the adsorption theory, taking into account lateral interactions between adparticles (see e.g. [8, 21]). By expanding $F_n(x)$ in the Taylor series in the neighborhood of x = 0 and keeping only the first term of the expansion, and expressing the adsorption-induced force $\vec{F}_n(x)$ in terms of the potential, $F_n(x) = -\frac{dV_n(x)}{dx}$, we get

$$V_n(x) \approx -\chi_n x, \quad n = 1, 2, \tag{1}$$

where

$$\chi_n = -\frac{\mathrm{d}V_n(x)}{\mathrm{d}x}\bigg|_{x=0}$$

is the constant adsorption-induced force acting on the adsorption site occupied by an adparticle of species n.

We introduce the dimensionless quantity $G = \chi_2/\chi_1$, which is positive or negative for parallel (sign $\chi_1 = \text{sign } \chi_2$) or antiparallel (sign $\chi_1 = -\text{sign } \chi_2$) adsorption-induced forces, respectively.

By disregarding the internal motions in the adparticle–adsorption site system, i.e. considering the motion of the bound adsorption site as a whole, and taking into account a change in the mass of the oscillator in adsorption within the framework of this approximation, we obtain the following equation of motion of an oscillator of variable mass under the action of the adsorption-induced force:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(m_{\mathrm{eff}}(\Theta)\frac{\mathrm{d}x}{\mathrm{d}t}\right) + \alpha \frac{\mathrm{d}x}{\mathrm{d}t} + \varkappa x = \chi_1 \,\theta_1 + \chi_2 \,\theta_2, \qquad (2)$$

where \varkappa is the restoring force constant, α is the friction coefficient, $m_{\text{eff}}(\Theta) = m_0 + m_1 \theta_1 + m_2 \theta_2$ is the effective mass of the oscillator that varies in adsorption, m_n is the mass of a gas particle of species *n* and the symbol $\Theta \equiv \{\theta_1, \theta_2\}$ denotes a collection of the surface coverages. Since $\theta_n \leq 1$, the effective mass of the oscillator is less than $M = m_0 + m_1 + m_2$.

It follows from equation (2) that, due to adsorption, the equilibrium position of the oscillator shifts from x = 0 (for a vacant adsorption site) to a new position $x^{eq}(\Theta)$ defined by the relation

$$x^{\text{eq}}(\Theta) = x_1^{\text{eq}}(\theta_1) + x_2^{\text{eq}}(\theta_2),$$
 (3)

where $x_n^{eq}(\theta_n) = x_n^{max} \theta_n$ is the equation for determination of the equilibrium position of the oscillator in the adsorption of a one-component gas of species *n* and $x_n^{max} \equiv x_n^{eq}(1) = \chi_n/\varkappa$ is the maximum stationary displacement of the oscillator from its nonperturbed equilibrium position x = 0 in the case of total surface coverage ($\theta_n = 1$).

Within the framework of the used approximation, the forces of lateral interactions between adparticles are parallel to the adsorbent surface and the adsorption-induced forces $\vec{F}_n(x)$ are perpendicular to the surface, which means that the forces $\vec{F}_n(x)$ are caused by the interaction of bound adsorption sites with neighboring subsurface atoms of the adsorbent. Nevertheless, the lateral interactions between adparticles affect the adsorption-induced force $\vec{F}(x, t)$ (and, hence, a normal displacement of the plane of adsorption sites) via the surface coverages θ_1 and θ_2 .

In the Langmuir theory of kinetics on a nondeformable adsorbent ($\chi_n = 0, n = 1, 2$) neglecting interactions between adparticles, the rate constants for adsorption and desorption k_n^a and k_n^d of particles of species *n*, respectively, do not depend on the concentration of particles in the gas phase and are defined by the Arrhenius relations

$$k_n^{\rm a} = k_n^{\rm +} \exp\left(-\frac{E_n^{\rm a}}{k_{\rm B}T}\right), \quad k_n^{\rm d} = k_n^{\rm -} \exp\left(-\frac{E_n^{\rm d}}{k_{\rm B}T}\right), \quad n = 1, 2,$$
(4)

where E_n^a and E_n^d are the activation energies for adsorption and desorption, respectively, k_n^+ and k_n^- are the pre-exponential factors, *T* is the absolute temperature and k_B is the Boltzmann constant.

The Hamiltonian of the adparticle-adsorbent system contains the term $-\chi_1 x N_1 - \chi_2 x N_2$ caused by the adsorbent deformation in adsorption due to the adsorption-induced force field $\vec{F}(x, t)$. This implies that an adparticle of species nis not only in a potential well of constant depth E_n^d but also in the adsorption-induced potential $V_n(x)$. Hence, for parallel adsorption-induced forces, an adparticle of any species is in a deeper potential well than on a nondeformable adsorbent. As a result, in the case at hand, for desorption of an adparticle of species n, it must get an energy greater than E_n^d by the value $|V_n(x)| = \chi_n x$, which can be regarded as the increment of the activation energy for desorption E_n^d of an adparticle of species n caused by the adsorbent deformation. For antiparallel adsorption-induced forces, the additions $\chi_n x$ to the activation energies for desorption E_n^d of adparticles of different species n have opposite signs. Thus, the adsorbent deformation increases the activation energy for desorption of adparticles of one species and decreases the activation energy for desorption of adparticles of another species. Note that the quantities E_n^d and $\chi_n x$ can be interpreted as the first and second terms, respectively, of the Taylor series of the coordinate-dependent activation energy for desorption $E_n^d(x)$, i.e. $E_n^d(x) = E_n^d + \chi_n x + \cdots$. It is well known that lateral interactions between

It is well known that lateral interactions between adparticles essentially change adsorption isotherms of a binary gas mixture (see e.g. [20]). In the present paper, to illustrate that there is another factor (the adsorption-induced deformation of the adsorbent) leading to qualitative changes in isotherms of competitive adsorption of a two-component gas, we do not take into account lateral interactions between adparticles.

The adsorbent deformation in adsorption affects the desorption rates of adparticles and, hence, the surface coverage. Assuming that the pre-exponential factors k_n^- are not changed, we obtain the following expression for the rate coefficients for desorption:

$$k_n^{\rm d}(x) = k_n^{\rm d} \exp\left(-\frac{\chi_n x}{k_{\rm B}T}\right).$$
 (5)

Thus, the rate coefficients for desorption (5) are coordinate-dependent functions, and gas particles are adsorbed on the surface whose adsorption characteristics vary with time.

According to (5), for G > 0, the desorption rates of adparticles of both species decrease due to the adsorbent

deformation in adsorption. For G < 0, the joint action of adparticles of both species on the adsorbent leads to the opposite results: the desorption rate of adparticles decreases for one species and increases for another.

With regard to variations in the adsorption properties of the adsorbent in adsorption, the kinetics of the surface coverages are described by the equations

$$\frac{\mathrm{d}\theta_n}{\mathrm{d}t} = k_n^{\mathrm{a}} C_n \,\theta_0 - k_n^{\mathrm{d}} \,\theta_n \,\exp\left(-\frac{\chi_n \,x}{k_{\mathrm{B}}T}\right), \quad n = 1, 2, \qquad (6)$$

where C_n is the concentration of gas particles of species n that is kept constant, $\theta_0 = 1 - \theta_+ = N_0(t)/N$ is the vacant part of the adsorbent surface, $\theta_+ = \theta_1 + \theta_2 = N_b(t)/N$ is the surface coverage by adparticles of both species, $N_b(t) = N_1(t) + N_2(t)$ and $N_0(t)$ are, respectively, the numbers of occupied and vacant adsorption sites at the time t, and $N_b(t) + N_0(t) = N$.

By setting in (6) $\chi_n = 0$, we obtain the known system of two linear equations that describes the Langmuir kinetics of adsorption of a two-component gas [18].

By introducing the dimensionless coordinate of oscillator $\xi = x/x_1^{\text{max}}$, we obtain the following autonomous system of three nonlinear differential equations that describes the kinetics of the surface coverages and the normal displacement of adsorption sites in localized adsorption with regard to variations in adsorption properties of the adsorbent in adsorption:

$$\begin{cases} \frac{d\theta_n}{dt} = k_n^{a} C_n \,\theta_0 - k_n^{d} \,\theta_n \exp\left(-\frac{g_n}{G_n} \,\xi\right), & n = 1, 2, \\ \frac{d}{dt} \left(m_{\text{eff}}(\Theta) \frac{d\xi}{dt} \right) + \alpha \frac{d\xi}{dt} = \varkappa \left(\theta_1 + G \,\theta_2 - \xi \right). \end{cases}$$
(7)

Here, the dimensionless quantity (called a coupling parameter of adparticles of species n)

$$g_n = |V_n|/k_{\rm B}T, \quad n = 1, 2$$
 (8)

is the maximum increment of the activation energy for desorption of adparticles of species *n* (normalized by $k_{\rm B} T$) due to the adsorbent deformation in adsorption of a one-component gas of species *n*, $V_n \equiv V_n(x_n^{\rm max}) = -\chi_n^2/\varkappa$, $G_1 = 1$, $G_2 \equiv G$, $g_2 = g_1 G^2$.

By setting in (7) $C_2 = 0$ and $\theta_2 = 0$, we obtain the system of two differential equations that describes the kinetics of the amount of a one-component gas of species 1 adsorbed on a deformable adsorbent [27].

For a given value of ξ , the average coordinate-dependent residence times of adparticles on the surface of a deformable adsorbent $\tau_n^{d}(\xi) = 1/k_n^{d}(\xi)$, n = 1, 2

$$\tau_1^{d}(\xi) = \tau_1^{d} \exp(g_1 \xi), \quad \tau_2^{d}(\xi) = \tau_2^{d} \exp(g_1 G \xi) \quad (9)$$

increase for G > 0 compared to the classical residence times

$$\tau_n^{\rm d} = \frac{1}{k_n^{\rm d}}, \quad n = 1, 2$$
 (10)

and, furthermore, the greater the displacement of the adsorption sites from their nonperturbed equilibrium position, the greater the increase. Since the residence time of adparticles with greater value of $|\chi_n|$ increases more, the

surface is more intensively occupied by particles of this species and this process rapidly grows with ξ . By denoting the ratio of the residence times of adparticles of different species on the adsorbent surface by

$$R(\xi) = \frac{\tau_2^{\rm d}(\xi)}{\tau_1^{\rm d}(\xi)} \tag{11}$$

we obtain

$$R(\xi) = R_0 w(\xi),$$
 (12)

where

$$R_0 \equiv R(0) = \frac{\tau_2^{\rm d}}{\tau_1^{\rm d}}$$
 (13)

is the ratio of the residence times of adparticles of different species on the surface of a nondeformable adsorbent and the quantity

$$w(\xi) = \exp\left(g_1\left(G-1\right)\xi\right) \tag{14}$$

characterizes a variation in ratio (13) due to the different actions of adparticles of both species on the adsorbent. In the special case of an identical action of all adparticles on the adsorbent ($\chi_1 = \chi_2$), we have $w(\xi) = 1$. According to (14), for G > 1, the quantity $w(\xi)$ can reach large values, which essentially affects the surface coverages θ_1 and θ_2 .

Expressions (9), (11), (12) and (14) are also true for G < 0. However, in this case, the adsorbent deformation caused by the joint action of adparticles of both species leads to an increase in the residence time of adparticles of one species and a decrease in the residence time of adparticles of other species compared to the classical residence times (10).

3. Stationary case

3.1. General relations

In the stationary case, system (7) is reduced to the system

$$\begin{cases} \ell_1 = \frac{\theta_1}{\theta_0} \exp\left(-g_1\,\xi\right), \\ \ell_2 = \frac{\theta_2}{\theta_0} \exp\left(-g_1\,G\,\xi\right), \\ \xi = \theta_1 + G\,\theta_2, \end{cases}$$
(15)

where $\ell_n = C_n K_n$ is the dimensionless concentration of gas particles of species *n* and $K_n = k_n^a/k_n^d$ is the adsorption equilibrium constant for a one-component gas of species *n* in the linear case ($\chi_n = 0$).

After simple transformations, we obtain the following expressions for the surface coverages:

$$\theta_1 = \frac{\xi}{1 + G S(\xi)},\tag{16}$$

$$\theta_2 = S(\xi) \,\theta_1 \tag{17}$$

as functions of the coordinate ξ , which is determined from the transcendental equation

$$\ell_1 = \frac{\xi \, \exp\left(-g_1\,\xi\right)}{D(\xi)},\tag{18}$$

where

$$D(\xi) = 1 - \xi + (G - \xi) S(\xi), \tag{19}$$

$$S(\xi) = \frac{\theta_2}{\theta_1} = S_0 w(\xi), \qquad (20)$$

$$S_0 \equiv S(0) = \frac{\ell_2}{\ell_1}.$$
 (21)

Thus, the problem under study is reduced to the investigation of the equilibrium position of the oscillator ξ in an adsorption-induced force field, i.e. dependence of a solution of equation (18) on the control parameters ℓ_1 , χ_1 and ℓ_2 , χ_2 . In what follows, as control parameters, we use ℓ_1 , g_1 (for particles of species 1) and S_0 , G (for particles of species 2) equal to, respectively, ℓ_2 and χ_2 normalized by ℓ_1 and χ_1 . For the classical adsorption of a binary gas mixture, the quantity S_0 for $C_2 = C_1$, called the separation factor [19, 22] (or the adsorbent selectivity of species 2 in relation to species 1 [21, 32]), is independent of the gas concentration. Thus, $w(\xi)$ characterizes the deviation of the quantity $S(\xi)$ from its classical analogue S_0 due to the adsorbent deformation in adsorption.

To pass to the case of adsorption of a one-component gas of species 1, we set $C_2 = 0$ in (16)–(21), which yields $\xi = \theta_1$ and the following equation for θ_1 on a deformable adsorbent [27]:

$$\ell_1 = \frac{\theta_1}{1 - \theta_1} \exp\left(-g_1 \theta_1\right). \tag{22}$$

According to (20), the quantity $S(\xi)$ depends on both the dimensional concentrations of gas particles of both species and the adsorption-induced forces.

Passing in relations (14) and (16)–(20) to the limit $\chi_1, \chi_2 \rightarrow 0$, we obtain the classical extended Langmuir (Markham–Benton) isotherms of a binary gas mixture [10, 18, 21]

$$\theta_n^{\rm L} = \frac{\ell_n}{1 + \ell_1 + \ell_2}, \quad n = 1, 2$$
(23)

and $\lim_{\chi_1, \chi_2 \to 0} S(\xi) = S_0$. Since the adsorbent surface is more intensively occupied by gas particles with greater dimensionless concentration, for $S_0 \ll 1$, we can neglect the presence of particles of species 2 in the binary gas mixture, and the problem under study can be regarded as the problem of adsorption of a one-component gas.

It follows from (20) that $S(\xi)$ is equal to S_0 only for $\chi_1 = \chi_2$. In this special case, the adsorbent deformation in adsorption leads to an increase in the numbers of adparticles of each species not changing their ratio S_0 .

For $\chi_1 \neq \chi_2$, the quantity $S(\xi)$ nonlinearly depends on the concentrations ℓ_1 and ℓ_2 and the parameters g_1 and G, and the problem of neglect of gas particles of the second species in a binary gas mixture in adsorption for $S_0 \ll 1$ remains. In the general case, to substantiate the passage from two-component adsorption to one-component adsorption, it is necessary to investigate in detail the behavior of $S(\xi)$ as a function of the control parameters in the entire range of their variation. Nevertheless, several qualitative conclusions can be drawn without awkward calculations. To this end, for $\chi_1 \neq \chi_2$, we consider the case of the total coverage ($\theta_+ = 1$), which is realized for large (infinite, in the limit) concentrations of gas particles provided that $S_0 \neq 0$. By using relations (16)–(20),

we obtain the following asymptotic values of the surface coverages $\theta_n^a = \lim_{\ell_1 \to \infty} \theta_n$, n = 1, 2:

$$\theta_1^a = \frac{G - \xi^a}{G - 1}, \quad \theta_2^a = \frac{\xi^a - 1}{G - 1},$$
(24)

where ξ^{a} is a root of the equation

$$D(\xi) = 0 \tag{25}$$

which belongs to the interval (1, G) if G > 1 or (G, 1) if G < 1. Since the concentration ℓ_1 is positive, the coordinate ξ tends to its asymptotic value ξ^a in a half neighborhood of the point ξ^a where sign $D(\xi) = \text{sign } \xi$, which yields

$$\lim_{\xi \to \xi^a} \ell_1(\xi) = +\infty.$$
 (26)

By using (24), we obtain the simple expression for the asymptotic ratio of surface coverages

$$S(\xi^{a}) \equiv \frac{\theta_{2}^{a}}{\theta_{1}^{a}} = \frac{\xi^{a} - 1}{G - \xi^{a}}.$$
 (27)

Thus, for the total coverage, under the condition

$$\xi^{a} > \frac{G+1}{2}$$
 if $G > 1$ or $\xi^{a} < \frac{G+1}{2}$ if $G < 1$
(28)

the number of adparticles of species 2 is greater than the number of adparticles of species 1 even if $S_0 \ll 1$, which indicates the necessity of taking account of particles of both species in problems of adsorption of binary gas mixtures. In what follows, the realization of condition (28) for $S_0 \ll 1$ will be shown for specific systems.

For given values of g_1 , G and S_0 , equation (25) can have several roots that belong to the above-mentioned interval and satisfy condition (26). In this case, the quantities ξ^a and θ_n^a have an additional subscript indicating the number of the root, and the functions $\xi(\ell_1)$ and $\theta_n(\ell_1)$ have several horizontal asymptotes in the limit $\ell_1 \rightarrow +\infty$.

Analysis shows that, for $G \neq 1$, the function $\xi(\ell_1)$ has three horizontal asymptotes $\xi = \xi_1^a$, $\xi = \xi_2^a$ and $\xi = \xi_3^a$ if $g_1 > g_c^a$, where $g_c^a = 4/(G-1)^2$, and $S_0 \in (I_-^a, I_+^a)$, where $I_{\pm}^a = S_{\pm}^a$ if G > 1 or $I_{\pm}^a = S_{\pm}^a$ if G < 1

$$S_{\pm}^{a} = \frac{1 \mp w_{a} \operatorname{sign}(G-1)}{1 \pm w_{a} \operatorname{sign}(G-1)} \exp(2 q_{a} \beta_{\pm}),$$

$$w_{a} = \sqrt{1 - \frac{1}{q_{a}}}, \quad q_{a} = \frac{g_{1}}{g_{c}^{a}},$$

$$\beta_{\pm} = \beta \pm w_{a} \operatorname{sign}(G - 1), \quad \beta = \frac{1 + G}{1 - G}.$$
(29)

For the interval $[I_{-}^{a}, I_{+}^{a}]$, its width $I_{a}(g_{1}, G) = I_{+}^{a} - I_{-}^{a}$ and the coordinate of its center $S^{a}(g_{1}, G) = (S_{+}^{a} + S_{-}^{a})/2$ are equal to

$$I_{a}(g_{1},G) = 2\{(2q_{a}-1) \sinh h - h \cosh h\} (S_{c}^{a})^{q_{a}}, \quad (30)$$

$$S^{a}(g_{1}, G) = \{(2q_{a} - 1) \cosh h - h \sinh h\} (S^{a}_{c})^{q_{a}}, \quad (31)$$

where $h = 2 w_a q_a = 2 \sqrt{q_a(q_a - 1)}$ and $S_c^a = \exp(2\beta)$ is the critical value of S_0 for which the interval $[I_-^a, I_+^a]$ degenerates

into a point $(S_+^a = S_-^a = S_c^a)$ for $g_1 = g_c^a$. The interval $[I_-^a, I_+^a]$ exists for $g_1 > g_c^a$ and lies from the left (if G > 1) or from the right (if $G \in [0, 1)$) of S_c^a ; for G < 0, depending on $q_a > 1$, the interval can both contain and not contain S_c^a .

If the coupling parameter g_1 is close to the critical g_c^a , i.e. $q_a = 1 + \varepsilon$, $0 < \varepsilon \ll 1$, then

$$I_{\rm a}(g_1,G) \approx \frac{8}{3} \,\varepsilon^{3/2} \,S^{\rm a}_{\rm c}, \quad S^{\rm a}(g_1,G) \approx (1+2\beta\,\varepsilon) \,S^{\rm a}_{\rm c}. \tag{32}$$

For a very strong coupling, $g_1 \gg g_c^a (q_a \gg 1)$

$$I_{a}(g_{1},G) \approx 2 S^{a}(g_{1},G), \quad S^{a}(g_{1},G) \approx \frac{1}{8q_{a}} \exp\left(\frac{4q_{a}}{1-G}\right).$$
(33)

For $S_0 \notin [I_-^a, I_+^a]$, the function $\xi(\ell_1)$ has only one horizontal asymptote $\xi = \xi_1^a$, whereas, for $S_0 \in (I_-^a, I_+^a)$, it has three horizontal asymptotes. Furthermore, the appearance of two additional asymptotes and their specific features essentially depend on the value of G.

For G > 1, as S_0 increases from a value less than S_{-}^a , for $S_0 = S_-^a + 0$, there appear two infinitely close asymptotes $\xi = \xi_2^a$ and $\xi = \xi_3^a$ above the asymptote $\xi = \xi_1^a (\xi_1^a < \xi_2^a < \xi_3^a)$; furthermore, the asymptote $\xi = \xi_3^a$, along with the asymptote $\xi = \xi_1^a$, is stable and the asymptote $\xi = \xi_2^a$ is unstable, which means that they are, respectively, asymptotes of the corresponding stable and unstable branches of the function $\xi(\ell_1)$. In the limiting case $S_0 = S_-^a$, the asymptotes $\xi =$ ξ_2^a and $\xi = \xi_3^a$ coalesce into one line $\xi = \xi_-^a$, where $\xi_-^a =$ $\beta_{-}(1-G)/2$, which is already not an asymptote of $\xi(\ell_1)$ because $\ell_1(\xi)$ does not satisfy condition (26) for $\xi = \xi_{-}^a$. The distance between the asymptotes $\xi = \xi_2^a$ and $\xi = \xi_3^a$ increases with $S_0 \in (S_-^a, S_+^a)$. Moreover, the unstable $\xi = \xi_2^a$ and stable $\xi = \xi_1^a$ asymptotes approach each other and, for $S_0 = S_+^a$, coalesce into one doubly degenerate asymptote $\xi = \xi_{+}^{a}$, where $\xi_{\pm}^{a} = \beta_{\pm} (1 - G)/2$, which, for $S_{0} > S_{\pm}^{a}$, disappears, and the function $\xi(\ell_1)$ again has one asymptote but $\xi = \xi_3^a$.

For G < 1, the function $\xi(\ell_1)$ has three horizontal asymptotes if $S_0 \in (S_+^a, S_-^a)$. However, its behavior with variation in S_0 differs from that considered above for G >1. For $G \in [0, 1)$, as S_0 increases, for $S_0 = S_+^a$, the doubly degenerate asymptote $\xi = \xi_+^a$ appears below the asymptote $\xi = \xi_1^a$. As S_0 negligibly increases, this asymptote splits into two infinitely close asymptotes: stable $\xi = \xi_3^a$ and unstable $\xi = \xi_2^a$ ($\xi_1^a > \xi_2^a > \xi_3^a$). As $S_0 \in (S_+^a, S_-^a)$ increases, the distance between the asymptotes $\xi = \xi_2^a$ and $\xi = \xi_3^a$ grows and the unstable $\xi = \xi_2^a$ and stable $\xi = \xi_1^a$ asymptotes approach each other and, for $S_0 = S_-^a$, coalesce into one line $\xi = \xi_-^a$, which is already not an asymptote of the function $\xi(\ell_1)$ because $\ell_1(\xi)$ does not satisfy condition (26) for $\xi = \xi_-^a$. As a result, for $S_0 > S_-^a$, the function $\xi(\ell_1)$ again has one asymptote but $\xi = \xi_3^a$.

Thus, for $G \ge 0$, the function $\xi(\ell_1)$ has one horizontal doubly degenerate asymptote $\xi = \xi_+^a$ if the value of S_0 coincides with the right end point (for G > 1) or the left end point (for $G \in [0, 1)$) of the interval $[I_-^a, I_+^a]$.

Asymptotes of the function $\xi(\ell_1)$ for G < 0 are investigated in [35].

According to (16) and (17), for $S_0 \in (I^a_-, I^a_+)$, the functions $\theta_1(\ell_1)$ and $\theta_2(\ell_1)$ also have three horizontal asymptotes $\theta_1 = \theta^a_{1,k}$ and $\theta_2 = \theta^a_{2,k}$, k = 1, 2, 3, two of which

are stable and one is unstable. At the end points of this interval, the doubly degenerate asymptotic values $\theta_{1,-}^{a}$ and $\theta_{2,-}^{a}$ (for $S_0 = S_{-}^{a}$) or $\theta_{1,+}^{a}$ and $\theta_{2,+}^{a}$ (for $S_0 = S_{+}^{a}$) of the surface coverages θ_1 and θ_2 are equal to

$$\theta_{1,\pm}^{a} = \frac{1 \pm w_{a} \operatorname{sign}(G-1)}{2}, \quad \theta_{2,\pm}^{a} = \frac{1 \mp w_{a} \operatorname{sign}(G-1)}{2}$$
(34)

and $|\theta_{1,\pm}^a - \theta_{2,\pm}^a| = w_a$ increases with the coupling parameter g_1 . Since only the surface coverages (34) consistent with condition (26) have a physical meaning, we obtain that, for $G \ge 0$, these quantities are $\theta_{1,+}^a$ and $\theta_{2,+}^a$, which yields $\theta_{1,+}^a > \theta_{2,+}^a$ for G > 1 and $\theta_{1,+}^a < \theta_{2,+}^a$ for $G \in [0, 1)$.

In the special case $g_1 = g_c^a$ ($S_0 = S_c^a$), $\xi_+^a = \xi_-^a \equiv \xi_c^a = (1+G)/2$, whereas $\theta_{1,+}^a = \theta_{1,-}^a \equiv \theta_c^a$ and $\theta_{2,+}^a = \theta_{2,-}^a \equiv \theta_c^a$, where $\theta_c^a = 1/2$, are equal to each other and, unlike ξ_c^a , independent of *G*.

3.2. Identical action of adparticles on the adsorbent: $\chi_1 = \chi_2$

In this simplest case, $g_1 = g_2 \equiv g$, G = 1, and the required quantities ξ and θ_n are defined only by one quantity θ_+ ,

$$\xi = \theta_+, \qquad \theta_1 = \frac{\theta_+}{1 + S_0}, \qquad \theta_2 = S_0 \,\theta_1.$$
 (35)

The surface coverage θ_+ is a solution of the equation

$$\ell_{+} = \frac{\theta_{+}}{1 - \theta_{+}} \exp\left(-g \,\theta_{+}\right),\tag{36}$$

where

$$\ell_{+} = \ell_{1} + \ell_{2} = (1 + S_{0}) \,\ell_{1} \tag{37}$$

is the summary dimensionless concentration of gas particles.

Since equation (36) coincides with the equation for one-component adsorption (22) with replacements of θ_1 by θ_+ and ℓ_1 by ℓ_+ , the problem of adsorption of a two-component gas is reduced to the problem of adsorption of a one-component gas with the dimensionless concentration l_+ . This enables us to directly use the results in [27] for the one-component adsorption.

First, consider the case of a small coupling parameter, $g \ll 1$. By using (35) and (36), we get

$$\theta_n \approx \theta_n^{\rm L} \left\{ 1 + g \, \frac{\ell_+}{(1+l_+)^2} \right\}, \quad n = 1, 2.$$
(38)

Since the second term on the right-hand side of (38) is positive, the adsorbent deformation in adsorption increases the number of adparticles of both species. This result agrees with the general conclusion presented below of an increase in the number of adparticles due to the adsorbent deformation, which is true for any value of g. Indeed, by rewriting (36) in the form

$$\frac{\theta_+}{1-\theta_+} = \ell_+ \exp\left(g\,\theta_+\right) \tag{39}$$

and taking into account that the quantities $\theta_+/(1-\theta_+)$ and ℓ_+ are equal to the ratios of the number of bound adsorption sites to the number of vacant adsorption sites, respectively, with and without regard for the adsorbent deformation in adsorption, we immediately establish that the surface coverage θ_+ is greater than that in the Langmuir case for

any gas concentration. The difference between the number of adparticles in the nonlinear $(g \neq 0)$ and linear (g = 0) cases increases with the coupling parameter g.

By using analysis of adsorption isotherms in [27], we obtain that θ_+ essentially depends on the values of g. For $g < g_c = 4$, as in the Langmuir case, the system is monostable: there is a single-valued correspondence between the concentration ℓ_+ and the surface coverage θ_+ . For $g > g_c$, the situation cardinally changes: if $\ell_+ \not\in [\ell_{+,1}^b, \ell_{+,2}^b]$, where $\ell_{+,1}^b$ and $\ell_{+,2}^b$ are the bifurcation concentrations whose explicit expressions are given below, then, as before, for every ℓ_+ , there is a unique θ_+ , whereas, for any $\ell_+ \in (\ell_{+,1}^b, \ell_{+,2}^b)$, there are three values of θ_+ : $\theta_{+,1} < \theta_{+,2} < \theta_{+,3}$. Furthermore, the stationary solutions $\theta_{+,1}$ and $\theta_{+,3}$ of system (7) are asymptotically stable and the stationary solution $\theta_{+,2}$ is unstable.

If the concentration $\ell_+ \in [\ell_{+,1}^b, \ell_{+,2}^b]$ tends to the end point $\ell_{+,1}^b$ (or $\ell_{+,2}^b$) of the interval, then the stable $\theta_{+,3}$ (or $\theta_{+,1}$) and unstable $\theta_{+,2}$ solutions approach each other and, in the limit $\ell_+ = \ell_{+,1}^b$ (or $\ell_+ = \ell_{+,2}^b$), coalesce into the two-fold solution $\theta_{+,1}^b$ (or $\theta_{+,2}^b$) equal to

$$\theta_{+,1}^{b} = \frac{1+w_{+}}{2} \quad \text{or} \quad \theta_{+,2}^{b} = \frac{1-w_{+}}{2},$$
(40)

where the quantity

$$w_{+} = \sqrt{1 - \frac{4}{g}} \tag{41}$$

is the width of the interval of instability of θ_+ symmetric about 1/2.

The bifurcation concentrations $\ell_{+,1}^{b}$ and $\ell_{+,2}^{b}$ for which the dynamical system (7) has two stationary solutions, one of which $(\theta_{+,1}^{b} \text{ or } \theta_{+,2}^{b})$ is two-fold, are equal to [27]

$$\ell^{\rm b}_{+,k} = \left(g \,\theta^{\rm b}_{+,k} - 1\right) \,\exp\left(-g \,\theta^{\rm b}_{+,k}\right), \quad k = 1, 2. \tag{42}$$

The bifurcation concentrations $\ell^{b}_{1,k}$, k = 1, 2, are defined by $\ell^{b}_{+,k}$ with the use of relation (37).

Thus, for $g > g_c$, there is an interval of values of ℓ_+ whose end points $\ell_{+,1}^b$, $\ell_{+,2}^b$ and width

$$I_{+}(g) = \ell_{+,2}^{b} - \ell_{+,1}^{b}$$

= $\left\{ (g-2) \sinh \frac{gw_{+}}{2} - gw_{+} \cosh \frac{gw_{+}}{2} \right\} \exp\left(-\frac{g}{2}\right)$ (43)

depend on the coupling parameter g so that the system is bistable if the concentration ℓ_+ belongs to this interval. We call this interval of concentrations ℓ_+ the bistability interval of the system. Note that relation (43) coincides with the width of the interval of pump intensity obtained in [36] for bistability of the function of a macromolecule in repeating cycles of reactions.

If the coupling parameter g is close to the critical g_c , i.e. $g = 4 (1 + \varepsilon), \ 0 < \varepsilon \ll 1$, then the bistability interval is very narrow

$$I_{+}(g) \approx \frac{8}{3} \exp(-2) \varepsilon^{3/2}$$
 (44)

the stationary solutions $\theta_{+,1}$, $\theta_{+,2}$ and $\theta_{+,3}$ are close to each other, and $w_+ \approx \varepsilon^{1/2}$. In the limit $\varepsilon \to 0$, the bistability



Figure 1. Adsorption isotherms of adparticles of species 1 for the one-component (curve 1) and two-component (curve 2) gas for g = 6, G = 1, $S_0 = 0.5$.

interval disappears and three stationary solutions coalesce into the three-fold solution $\theta_+^c = 1/2$. Thus, for g = 4 and $\ell_+ = \ell_+^c = \exp(-2) \approx 0.135$, the dynamical system (7) has one three-fold stationary solution.

The comparison of the *S*-shaped adsorption isotherms of adparticles of species 1 in figure 1 for the one-component (curve 1) and two-component (curve 2) gas for $g = 6 > g_c$ clearly illustrates the influence of particles of species 2 in the gas mixture on the behavior of the surface coverage θ_1 . In this and subsequent figures for the surface coverage $\theta_n(\ell_1)$ and the equilibrium position of oscillator $\xi(\ell_1)$, the parts of curves corresponding to stable and unstable stationary solutions are shown, respectively, by solid and broken lines.

The obtained adsorption isotherms essentially differ from the classical Langmuir isotherms. At the same time, the presence of particles of species 2 in the gas phase leads only to quantitative changes in adsorption isotherms of a one-component gas for a deformable adsorbent [27]: a decrease in the amount of adsorbed substance and displacement and a decrease in the bistability interval of the system, which completely agrees with relations (35), (37) and (42).

As the concentration ℓ_1 increases from zero, the surface coverage θ_1 increases along the lower stable branch of the isotherm and the increment of θ_1 is determined by both an increase in the gas concentration and a change in the adsorption properties of the adsorbent due to its deformation. Since the lower stable branch of the isotherm ends at $\ell_1 =$ $\ell_{1,2}^{b}$, a negligible excess of the bifurcation concentration $\ell_{1,2}^{b}$ is accompanied by the jump of θ_{1} to the upper stable branch of the isotherm, i.e. a stepwise increase in the surface coverage solely due to a change in adsorption properties of the adsorbent. This transition can include many gas particles (furthermore, of both species) successively taking part in the process of adsorption-desorption on the same adsorption site. Thus, at this stage, some interaction between the particle leaving the adsorption site and the particle binding with it occurs.

A subsequent increase in the concentration ℓ_1 slightly affects the surface coverage θ_1 that varies along the upper stable branch because the majority of adsorption sites are already bound. In passing through the bifurcation concentration $\ell_{1,2}^b$, desorption of adparticles essentially decreases due to a considerable increase in their activation energy for desorption. As a result, for returning from the upper stable branch of the isotherm to its lower stable branch, the concentration ℓ_1 must be lower than $\ell_{1,2}^b$. As ℓ_1 decreases from a value greater than $\ell_{1,2}^b$, the surface coverage θ_1 decreases along the upper stable branch of the isotherm up to its end at $\ell_1 =$ $\ell_{1,1}^b$. In passing through the bifurcation concentration $\ell_{1,1}^b$, the surface coverage jumps down to the lower stable branch of the isotherm and then decreases along this branch.

The behavior of the surface coverage θ_1 versus ℓ_1 agrees with the principle of perfect delay [37, 38]: a system that is in a stable state at the initial time remains in this state with variation in a parameter (the concentration ℓ_1 in the case at hand) as long as the state exists.

According to (35), the specific features of adsorption isotherms are also true for the coordinate ξ characterizing the displacement of the plane of adsorption sites from its nonperturbed position. For example, the curves in figure 1 also describe the equilibrium position of the oscillator versus ℓ_1 in adsorption of a one-component and two-component gas if, instead of θ_1 , ξ (for one-component adsorption) and (2/3) ξ (for two-component adsorption) are laid off along the ordinate axis.

3.3. Equilibrium position of the oscillator

The equilibrium position of the oscillator $\xi(\ell_1)$ is a solution of equation (18). To analyze solutions of this equation, we plot the function $\ell_1(\xi)$ inverse to the required $\xi(\ell_1)$, i.e. the right-hand side of (18). The abscissas of the points of intersection of the graph of the function $\ell_1(\xi)$ with a horizontal line corresponding to the given concentration $\ell_1 > 0$ are solutions of equation (18). Thus, the problem under study is reduced to the investigation of the function $\ell_1(\xi) \ge 0$ depending on the control parameters g_1 , G and S_0 .

Points of possible finite local extrema of the function $\ell_1(\xi)$ are solutions of the equation

$$L(\xi; g_1, G, S_0) = 0, \tag{45}$$

where

$$L(\xi; g_1, G, S_0) = L_1(\xi; g_1) + G S(\xi) L_2(\xi; g_1, G)$$
(46)

the quantity

$$L_1(\xi; g_1) = 1 + g_1 \xi \ (\xi - 1) \tag{47}$$

is associated with adsorption of a one-component gas of species 1 and the quantity

$$L_2(\xi; g_1, G) = 1 + g_1 \xi \ (\xi - G) \tag{48}$$

is caused by the presence of particles of species 2 in the binary gas mixture.

In the special case where adparticles of species 2 do not affect the adsorbent deformation, $\chi_2 = 0$ (*G* = 0), equation (45) coincides with the equation

$$L_1(\xi; g_1) = 0 \tag{49}$$

Table 1. Control parameters for five-fold solutions.

	Control parameters				Solutions		
Number	$\overline{G^{but}}$	$g_1^{\rm but}$	ℓ_1^{but}	$S_0^{\rm but}$	ξ^{but}	$\theta_1^{\rm but}$	θ_2^{bu}
1	2	3	$4 \exp(-3)$	$\exp(-3)/4$	1	2/3	1/6
2	1/2	12	$\exp(-6)$	$4 \exp(3)$	1/2	1/6	2/3
3	-1	3	1/4	1	0	1/6	1/6

for points of possible extrema of $\ell_1(\xi)$ in adsorption of a one-component gas of species 1.

Note that equation (45) is also reduced to (49) in another special case investigated in section 3.2 of the identical action of all adparticles on the adsorbent, $\chi_1 = \chi_2$ (*G* = 1).

We denote real roots of equation (45) for $S_0 > 0$ by ξ_k^b , where k = 1, 2, ..., and call roots ξ_k^b for which the bifurcation concentrations $\ell_{1,k}^b = \ell_1(\xi_k^b) > 0$ bifurcation coordinates. By using (16), (17) and (45)–(48), for $G \neq 0, 1$, we obtain the following relations for the bifurcation surface coverages $\theta_{1,k}^b = \theta_1(\xi_k^b)$ and $\theta_{2,k}^b = \theta_2(\xi_k^b)$:

$$\theta_{1,k}^{\rm b} = \frac{L_2(\xi_k^{\rm b}; g_1, G)}{g_1 (1 - G)}, \quad \theta_{2,k}^{\rm b} = \frac{L_1(\xi_k^{\rm b}; g_1)}{g_1 G (G - 1)}.$$
 (50)

The function $\ell_1(\xi)$ has a finite local extremum at the point $\xi = \xi_k^{\rm b}$ if the function

$$L_{\rm c}(\xi; g_1, G) = 2\xi - 1 + (\xi - G) \ L_1(\xi; g_1) \tag{51}$$

is not equal to zero at this point. In this case, $\xi_k^{\rm b}$, $\theta_{1,k}^{\rm b}$, $\theta_{2,k}^{\rm b}$ are the components of the *k*th two-fold stationary solution of system (7). Otherwise, for

$$L_{\rm c}(\xi_k^{\rm b}; g_1, G) = 0 \tag{52}$$

the investigation of $\ell_1(\xi)$ at this point must be continued. By ξ_k^c , k = 1, 2, 3, we denote real roots of the cubic equation (52). Both the number of these roots and their values depend on g_1 and *G*. We call roots ξ_k^c for which the critical concentrations $\ell_{1,k}^c = \ell(\xi_k^c) > 0$ critical coordinates. The critical values of $S_0 > 0$ denoted by S_k^c are determined from (45) for $\xi = \xi_k^c$. The critical surface coverages $\theta_{1,k}^c$ and $\theta_{2,k}^c$ are defined by relations (50) with ξ_k^b replaced by ξ_k^c . Hence, ξ_k^c , $\theta_{1,k}^c$, $\theta_{2,k}^c$ are the components of the *k*th at least three-fold stationary solution of system (7).

The more detailed analysis shows that equation (18) has a maximum (five-fold) multiple root for three values $G^{\text{but}} = 2, 1/2, -1$ of the parameter G and the corresponding values of g_1 , ℓ_1 , S_0 . In the four-dimensional (4D) space of control parameters { ℓ_1 , S_0 , g_1 , G}, a point with coordinates ℓ_1^{but} , S_0^{but} , g_1^{but} , G^{but} (a butterfly-type catastrophe [37, 38]) gives a five-fold stationary solution of system (7). In the three-dimensional (3D) space of solutions { ξ , θ_1 , θ_2 }, this five-fold solution is a point with coordinates ξ^{but} , θ_1^{but} , θ_2^{but} . The values of the three five-fold stationary solutions of system (7) and the corresponding control parameters are given in table 1.

In the general case, the analysis of stationary solutions of system (7) depending on control parameters is a complicated problem. To investigate the problem, we proceed as follows: first, by fixing a value of *G*, we select a 3D subspace of control parameters $\{\ell_1, S_0, g_1\}$ from the original 4D space.

Among all 3D subspaces thus obtained, there are only three subspaces for $G = G^{\text{but}}$, each of which contains a unique point with coordinates ℓ_1^{but} , S_0^{but} , g_1^{but} , giving a five-fold stationary solution of system (7). Moreover, in these three cases, analytic expressions are relatively simple. Then, by using the results of the analysis of stationary solutions of system (7) in these special cases, we can draw the corresponding conclusions for other values of *G* for which system (7) does not have five-fold stationary solutions. Since the case of negative values of *G* is of interest in its own right, the case G = -1 is not investigated here. In view of the fact that the cases G = 2 and 1/2 are similar (see table 1), below, we consider the case G = 2.

3.4. Case G = 2

In this case, equation (52) has three roots

$$\xi_1^c = 1, \quad \xi_2^c \equiv \xi_+^c = 1 + q,$$

$$\xi_3^c \equiv \xi_-^c = 1 - q, \quad q = \sqrt{1 - \frac{3}{g_1}}$$
(53)

which are points of inflection of the function $\ell_1(\xi)$ and, furthermore, at the points $\xi = \xi_1^c$, and $\xi = \xi_2^c$, $d^3 \ell_1(\xi)/d\xi^3 \neq 0$ o, whereas, at the point $\xi = \xi_1^c$, $d^3 \ell_1(\xi)/d\xi^3 \neq 0$ if $g_1 \neq 3$ and $d^3 \ell_1(\xi)/d\xi^3 = d^4 \ell_1(\xi)/d\xi^4 = 0$, $d^5 \ell_1(\xi)/d\xi^5 \neq 0$ if $g_1 = 3$. According to (53), the function $\ell_1(\xi)$ has one point of inflection ξ_1^c if $g_1 < 3$ and three points of inflection if $g_1 > 3$; furthermore, only two of them $(\xi_1^c$ and $\xi_2^c)$ depend on the coupling parameter g_1 . This result essentially differs from the results of adsorption of a one-component gas or a two-component gas for G = 1 for which the function $\ell_1(\xi)$ has only one point of inflection, $\xi^c = 1/2$, for $g_1 = 4$. If $\lim_{g_1 \to 3+0}$, then the three roots (53) coalesce into one triple root.

The critical parameters $\ell_{1,k}^c$ and S_k^c (re-denoted as follows: $\ell_{1,2}^c \equiv \ell_{1,+}^c, \ell_{1,3}^c \equiv \ell_{1,-}^c, S_2^c \equiv S_+^c, S_3^c \equiv S_-^c)$ are equal to

$$\ell_{1,1}^{c} = 2(g_{1}-1) \exp(-g_{1}), \quad \ell_{1,\pm}^{c} = \frac{4}{g_{1}\xi_{\pm}^{c}-2} \exp(-g_{1}\xi_{\pm}^{c}),$$
(54)

$$S_1^c = \frac{\exp(-g_1)}{2(g_1 - 1)}, \qquad S_{\pm}^c = \frac{g_1\xi_{\pm}^c - 2}{4} \exp(-g_1\xi_{\pm}^c).$$
 (55)

Non-negativity of ℓ_1 and S_0 imposes the following restrictions on g_1 : $g_1 > 1$ for ξ_1^c and $g_1 \in [3, 4)$ for ξ_{\pm}^c . Thus, the function $\ell_1(\xi) \ge 0$ has three points of inflection only for $g_1 \in$ (3, 4) and, hence, an essential difference between adsorption isotherms of two-component and one-component gases are expected precisely in this range of values of g_1 . The quantities $\ell_{1,1}^c$, $\ell_{1,\pm}^c$ and S_1^c , S_{\pm}^c as functions of the coupling parameter g_1 are arranged as follows: $\ell_{1,+}^c > \ell_{1,-}^c > \ell_{1,1}^c$ and $S_1^c > S_+^c > S_-^c$ for any $g_1 \in (3, 4)$ and coincide ($\ell_{1,1}^c = \ell_{1,\pm}^c = \ell_1^{but} \approx 0.199$ and $S_1^c = S_{\pm}^c = S_0^{but} \approx 0.0124$) for $g_1 = 3$.

By substituting (54) and (55) into (50), we obtain the critical surface coverages $\theta_{n,k}^c$ (re-denoted as follows: $\theta_{n,2}^c \equiv \theta_{n,+}^c, \theta_{n,3}^c \equiv \theta_{n,-}^c$, where n = 1, 2)

$$\theta_{1,1}^{c} = 1 - \frac{1}{g_{1}}, \quad \theta_{1,\pm}^{c} = \frac{2}{g_{1}}, \quad \theta_{2,1}^{c} = \frac{1}{2g_{1}}, \quad \theta_{2,\pm}^{c} = \frac{g_{1}\xi_{\pm}^{c} - 2}{2g_{1}}.$$
(56)



Figure 2. Graphical solution of equation (18) for different values of S_0 : (a) $S_0 = 0.001$ (1), 0.003 (2), 0.005 (3); (b) $S_0 = S_-^c$ (1), 0.0055 (2), S_+^c (3); (c) $S_0 = 0.0057$ (1), 0.00575 (2), 0.0058 (3); (d) $S_0 = S_1^c$ (1), 0.007 (2), 0.01 (3); $G = 2, g_1 = 3.5$. Horizontal dashed lines correspond to constant values of the concentration ℓ_1 .

In the degenerate case $g_1 = 3$, we have $\theta_{1,1}^c = \theta_{1,\pm}^c = \theta_1^{but} = 2/3$ and $\theta_{2,1}^c = \theta_{2,\pm}^c = \theta_2^{but} = 1/6$.

In the case $g_1 = 3.5$ considered below, $\xi_+^c \approx 1.378$, $\xi_-^c \approx 0.622$ and $\ell_{1,1}^c \approx 0.151$, $\ell_{1,+}^c \approx 0.182$, $\ell_{1,-}^c \approx 0.161$, $S_1^c \approx 0.00604$, $S_+^c \approx 0.00568$, $c_-^c \approx 0.00502$.

The graphs of $\ell_1(\xi)$ for different values of S_0 are shown in figure 2. The required solutions ξ of equation (18) are the abscissas of the points of intersection of a dashed horizontal line corresponding to the given ℓ_1 with the graph of $\ell_1(\xi)$.

For low concentrations ℓ_2 such that $S_0 < S_-^c$, the curve of the function $\ell_1(\xi)$ intersects any horizontal line of the given ℓ_1 at one point, which gives a unique value of ξ for any ℓ_1 (figure 2(a)). An increase in S₀ is accompanied by an increase in the number of adparticles of species 2 and, hence, the effective adsorption-induced force F(x) acting on adsorption sites, which increases their displacement from the nonperturbed equilibrium position $\xi = 0$. For the least critical $S_0 = S_-^c$ (curve 1 in figure 2(b)), the function $\ell_1(\xi)$ has a point of inflection at $\xi = \xi_{-}^{c}$ and is equal to the critical concentration $\ell_{1,-}^{c}$ at this point. A negligible increase in S₀ leads to the deformation of the curve in the neighborhood of the point ξ_{-}^{c} so that a minimum and a maximum of $\ell_1(\xi)$ appear, equal to the bifurcation concentrations $\ell_{1,1}^{b}$ and $\ell_{1,2}^{b}$ ($\ell_{1,1}^{b} < \ell_{1,2}^{b} <$ $\ell_{1,-}^{c}$), respectively, at the points $\xi = \xi_1^{b}$ and $\xi = \xi_2^{b}$. As S_0 increases, the bifurcation concentrations $\ell^{b}_{1,1}$ and $\ell^{b}_{1,2}$ decrease and the width $I_{2,1} = \ell_{1,2}^{b} - \ell_{1,1}^{b}$ of the interval $[\ell_{1,1}^{b}, \ell_{1,2}^{b}]$, called the first bistability interval of the system, increases (cf $I_{2,1}$ for curves 2 and 3 in figure 2(b)). The situation is similar to that in the adsorption of a one-component gas [27] or a two-component gas for G = 1 if values of the coupling parameter are greater than critical: for $\ell_1 \notin [\ell_{1,1}^b, \ell_{1,2}^b]$, there is a single-valued correspondence between the concentration ℓ_1 and the coordinate ξ ; for any $\ell_1 \in (\ell_{1,1}^b, \ell_{1,2}^b)$, there are three values of the coordinate $\xi: \xi_1 < \xi_2 < \xi_3$; furthermore, the stationary solutions ξ_1 and ξ_3 of system (7) are asymptotically stable and the stationary solution ξ_2 is unstable. If the concentration $\ell_1 \in [\ell_{1,1}^b, \ell_{1,2}^b]$ tends to the end point $\ell_{1,1}^b$ (or $\ell_{1,2}^b$) of the interval, then the stable ξ_3 (or ξ_1) and unstable ξ_2 solutions approach each other and, in the limit $\ell_1 = \ell_{1,1}^b$ (or $\ell_1 = \ell_{1,2}^b$), coalesce into the two-fold solution ξ_1^b (or ξ_2^b). Thus, for $S_0 \in (S_-^c, S_+^c)$, the system is monostable if $\ell_1 \notin [\ell_{1,1}^b, \ell_{1,2}^b]$ and bistable if $\ell_1 \in [\ell_{1,1}^b, \ell_{1,2}^b]$.

For the second critical value $S_0 = S_+^c$ (curve 3 in figure 2(b)), the function $\ell_1(\xi)$ has a point of inflection at $\xi = \xi_+^c$ and is equal to the maximum critical concentration $\ell_{1,+}^c$ at this point. As $S_0 \in (S_+^c, S_1^c)$ increases, the behavior of $\ell_1(\xi)$ (figure 2(c)) is similar to that in figure 2(b) for $S_0 \in (S_-^c, S_+^c)$. First, the function changes the shape in the neighborhood of the point ξ_+^c so that $\ell_1(\xi)$ has a minimum and a maximum equal to the bifurcation concentrations $\ell_{1,3}^b$ and $\ell_{1,4}^b (\ell_{1,3}^b < \ell_{1,4}^c < \ell_{1,+}^c)$, respectively, at the points $\xi = \xi_3^b$ and $\xi = \xi_4^b$. This yields the second bistability interval $[\ell_{1,3}^b, \ell_{1,4}^b]$ of the system of width $I_{4,3} = \ell_{1,4}^b - \ell_{1,3}^b$ nonintersecting with the first. As S_0 increases, the bifurcation concentrations



Figure 3. Bifurcation curve for G = 2, $g_1 = 3.5$.

 $\ell_{1,3}^{b}$ and $\ell_{1,4}^{b}$ decrease and the width $I_{4,3}$ increases (cf $I_{4,3}$ for the curves in figure 2(c)). An increase in $S_0 \in (S_{+}^{c}, S_{1}^{c})$ leads, first, to the partial overlapping of the first and second bistability intervals and then to their complete overlapping, where the second bistability interval includes the first (curve 3 in figure 2(c)). In the case of overlapping bistability intervals, for any concentration $\ell_1 \in (\ell_{1,1}^{t}, \ell_{1,2}^{t})$, where $[\ell_{1,1}^{t}, \ell_{1,2}^{t}] = [\ell_{1,1}^{b}, \ell_{1,2}^{b}] \cap [\ell_{1,3}^{b}, \ell_{1,4}^{b}], \ell_{1,1}^{t} = \max(\ell_{1,1}^{b}, \ell_{1,3}^{b}),$ $\ell_{1,2}^{t} = \min(\ell_{1,2}^{b}, \ell_{1,4}^{b})$, there are five values of the coordinate $\xi: \xi_1 < \xi_2 < \xi_3 < \xi_4 < \xi_5$; furthermore, the stationary solutions ξ_1 , ξ_3 and ξ_5 of system (7) are asymptotically stable and the stationary solutions ξ_2 and ξ_4 are unstable. Thus, for $\ell_1 \in [\ell_{1,1}^{t}, \ell_{1,2}^{t}]$, the system is tristable. We call the concentration interval $[\ell_{1,1}^{t}, \ell_{1,2}^{t}]$ a tristability interval of the system.

If the concentration $\ell_1 \in [\ell_{1,1}^t, \ell_{1,2}^t]$ tends to the end point of the interval, then a stable solution and an unstable solution approach each other and, in the limit $\ell_1 = \ell_{1,1}^t$ (or $\ell_1 = \ell_{1,2}^t$), coalesce into a two-fold solution. In this case, system (7) has four stationary solutions (two asymptotically stable, one unstable and one two-fold). For $\ell_1 = \ell_{1,1}^t$, the two-fold solution is ξ_1^b if $\ell_{1,1}^b > \ell_{1,3}^b$ or ξ_3^b if $\ell_{1,1}^b < \ell_{1,3}^b$. For $\ell_1 = \ell_{1,2}^t$, the two-fold solution is ξ_2^b if $\ell_{1,2}^b < \ell_{1,4}^b$ or ξ_4^b if $\ell_{1,2}^b > \ell_{1,4}^b$.

The arguments for a two-fold solution for the end points of the tristability interval must be corrected for two values of $S_0 \in (S_+^c, S_1^c)$ denoted by S_d and S_t and corresponding, respectively, to the equality of the lower (for $S_0 = S_d \approx$ 0.005 78) or upper (for $S_0 = S_t \approx 0.005$ 89) end points of the bistability intervals, i.e. the cases of equal minima $\ell_{1,1}^b =$ $\ell_{1,3}^b \equiv \ell_d^b \approx 0.155$ ($\ell_{1,1}^t = \ell_d^b$) or maxima $\ell_{1,2}^b = \ell_{1,4}^b \equiv \ell_t^b \approx$ 0.158 ($\ell_{1,2}^t = \ell_t^b$) of $\ell_1(\xi)$). For $\ell_{1,1}^t = \ell_d^b$ (or $\ell_{1,2}^t = \ell_t^b$), if the concentration $\ell_1 \in [\ell_{1,1}^t, \ell_{1,2}^t]$ tends to the end point ℓ_d^b (or ℓ_t^b) of the interval, then simultaneously two pairs of stable and unstable solutions approach each other and, in the limit $\ell_1 = \ell_d^b$ (or $\ell_1 = \ell_t^b$), coalesce into two two-fold solutions. In these two cases, system (7) has three stationary solutions (one asymptotically stable and two two-fold). As soon as ℓ_1 leaves the tristability interval, both two-fold solutions disappear and the system becomes monostable.

It is worth noting one more case where system (7) has one asymptotically stable and two two-fold stationary solutions. This case occurs for the value of $S_0 \in (S_+^c, S_1^c)$, denoted by S_u ($S_u \approx 0.005764$), for which two bistability intervals have only one common point ℓ_u^b such that $\ell_{1,2}^b = \ell_{1,3}^b \approx \ell_u^b \approx 0.1582$, i.e.

the maximum of $\ell_1(\xi)$ at $\xi = \xi_2^b$ is equal to the minimum of this function at $\xi = \xi_3^b$: $\ell_1(\xi_2^b) = \ell_1(\xi_3^b) \equiv \ell_u^b$. Unlike the cases considered above for two-fold solutions, in this case, a negligible variation (furthermore, in any side) in ℓ_1 from ℓ_u^b is accompanied by the disappearance of one two-fold solution and the splitting of the second into two (stable and unstable) solutions.

Three values— S_d , S_t and S_u —of $S_0 \in (S_+^c, S_1^c)$, for which the system has two two-fold solutions, are arranged as follows: $S_t > S_d > S_u$.

As $S_0 \in (S_+^c, S_1^c)$ increases, the first bistability interval decreases and the points ξ_1^b and ξ_4^b at which $\ell_1(\xi)$ has the minimum and the maximum, respectively, approach each other. For $S_0 = S_1^c$, the points coalesce into one ξ_1^c at which the function $\ell_1(\xi)$ has a point of inflection and is equal to the least critical concentration $\ell_{1,1}^c$ (curve 1 in figure 2(d)). For $S_0 > S_1^c$, the inflection of $\ell_1(\xi)$ disappears and the function has one minimum and one maximum at the points $\xi = \xi_3^b$ and $\xi = \xi_2^b$, respectively (curves 2 and 3 in figure 2(d)). Thus, for $S_0 > S_1^c$, the system has once bistability interval $[\ell_{1,3}^b, \ell_{1,2}^b]$ of width $I_{2,3} = \ell_{1,2}^b - \ell_{1,3}^b$.

For other values of $g_1 \in (3, 4)$, qualitative analysis of specific features of stationary solutions of system (7) can be made by using the behavior of the critical values of ℓ_1 and S_0 [35].

Specific features of the behavior of system (7) for G = 2 can be clearly illustrated by plotting a bifurcation surface, which is a set of multiple roots of equation (18), in the 3D space of control parameters $\{\ell_1, S_0, g_1\}$. Instead of this surface, we plot the bifurcation curve $\ell_1(S_0)$, which is the projection of the section of this bifurcation surface by a plane of a fixed value of g_1 onto the plane (S_0, ℓ_1) . To this end, by using (18) and (45), we obtain the following representation of this bifurcation curve in the parametric form, which is true for any $G \neq 0, 1$:

$$S_{0} = -\frac{1}{G} \frac{L_{1}(\xi; g_{1})}{L_{2}(\xi; g_{1}, G)} \frac{1}{w(\xi)},$$

$$\ell_{1} = \frac{G}{1-G} \frac{L_{2}(\xi; g_{1}, G) \exp(-g_{1}\xi)}{1+g_{1}(1-\xi)(G-\xi)}.$$
(57)

The bifurcation curve in figure 3 plotted for the same values of g_1 and G as in figure 2 has several singular points, which are shown in figure 3(b), where a part of the curve

is scaled up for the most interesting range $S_0 \in (S_-^c, S_1^c)$, $\ell_1 \in (\ell_{1,1}^c, \ell_{1,+}^c)$. The points $P_1 \equiv (S_1^c, \ell_{1,1}^c), P_+ \equiv (S_+^c, \ell_{1,+}^c),$ and $P_{-} \equiv (S_{-}^{c}, \ell_{1,-}^{c})$ are the cusps of the bifurcation curve corresponding to the points of inflection of the function $\ell_1(\xi)$ at $\xi = \xi_1^c$, ξ_2^c and ξ_2^c , respectively. The self-intersection points of the bifurcation curve $P_d \equiv (S_d, \ell_d^b), P_t \equiv (S_t, \ell_t^b)$ and $P_u \equiv (S_u, \ell_u^b)$ correspond to the system with two two-fold stationary solutions. For any point of the first quadrant of this plane lying outside the bifurcation curve, system (7) has one asymptotically stable stationary solution, i.e. it is a domain of monostability of the system. For a point lying in the curvilinear quadrangle $P_t P_u P_d P_1$, which is the domain of intersection of two curvilinear triangles $P_1 P_+ P_d$ and $P_1 P_- P_t$, system (7) has five stationary solutions (three asymptotically stable and two unstable), i.e. it is the domain of tristability of the system. If a point lies in one of the domains (the curvilinear triangles $P_t P_+ P_u$ and $P_u P_- P_d$ and the domain $B_t P_t P_1 P_d B_d$, B_t and B_d being symbolic notations for points of the upper and lower branches of the bifurcation curve, respectively, in the limit $S_0 \rightarrow \infty$), then system (7) has three stationary solutions (two asymptotically stable and one unstable), i.e. they are domains of bistability of the system. At any point of the bifurcation curve, except for the points of the boundary of the curvilinear quadrangle $P_t P_u P_d P_1$ and the singular points P_+ and P_- , system (7) has two stationary solutions (one asymptotically stable and one two-fold). At a nonvertex point of the boundary of the quadrangle $P_t P_u P_d P_1$, system (7) has four stationary solutions (three structurally stable-furthermore, two asymptotically stable and one unstable-and one two-fold). At the singular points P_d , P_t and P_u , system (7) has three stationary solutions (one asymptotically stable and two two-fold). At the singular points P_+ and P_- , system (7) has one three-fold stationary solution. At the singular point P_1 , system (7) has three stationary solutions (two asymptotically stable and one three-fold).

Motion in the plane (S_0, ℓ_1) along a line can be accompanied by the appearance of new solutions, the disappearance of existing solutions, and a change in solution stability in intersecting the bifurcation curve. This depends on both the point of intersection and the line itself if it intersects the bifurcation curve at a singular point and the direction of motion. Independently of the line, its intersection with the bifurcation curve at a nonsingular point is accompanied by the appearance/disappearance (depending on the direction of motion) of a pair of stationary (stable and unstable) solutions of system (7). In entering the domain $P_t P_+ P_u$ or $P_u P_- P_d$ through the cusp P_+ or P_- , respectively, a stable solution splits into three solutions (two stable and one unstable) and changes its stability. In entering the domain $P_t P_+ P_u P_1$ through the cusp P_1 , an unstable solution splits into three solutions (two unstable and one stable). In leaving these domains along a line passing through the cusp, three solutions (two stable and one unstable in the domains $P_t P_+ P_u$ and $P_u P_- P_d$ or two unstable and one stable in the domain $P_t P_+ P_u P_1$) coalesce into a three-fold solution at the cusp with its subsequent transformation outside the point into a simple stable (for the points P_+ and P_-) or unstable (for the point P_1) solution. In entering/leaving the domain of tristability $P_t P_u P_d P_1$ from/for the domain of monostability through the points P_d , P_t or P_u , which are unique common points of these domains,

two two-fold solutions simultaneously appear/disappear. If a line enters the domain $P_t P_+ P_u$ from the domain $P_u P_- P_d$ (or, conversely, enters the domain $P_u P_- P_d$ from the domain $P_t P_+ P_u$) through their common point P_u , then a stable solution and an unstable solution coalesce into a two-fold solution at the point P_u that disappears as it moves away from the point, whereas another two-fold solution appears at this point and then splits into a pair of stable and unstable solutions. A similar behavior of the system occurs in the motion from one domain of bistability to another through their common point (P_d for the domains of bistability $P_u P_- P_d$ and $B_t P_t P_1 P_d B_d$ or P_t for the domains of bistability $P_t P_+ P_u$ and $B_t P_t P_1 P_d B_d$).

The bifurcation curve for other values of $g_1 \in (3, 4)$ is similar to the curve in figure 3. As g_1 decreases, the triangles $P_u P_- P_d$ and $P_t P_+ P_u$ and the quadrangle, $P_t P_u P_d P_1$ decrease and, in the limit $g_1 \rightarrow 3$, shrink to the point $P_{but} \equiv (S_0^{but}, \ell_1^{but})$, and tristability of the system is impossible for $g_1 \leq 3$. As g_1 increases, the triangles $P_u P_- P_d$ and $P_t P_+ P_u$ elongate toward the ordinate axis and along it, respectively, and, furthermore, in the limit $g_1 \rightarrow 4$, the vertex P_- of the triangle $P_u P_- P_d$ lies on the ordinate axis $(P_- \equiv (0, \ell_1^c))$, where $\ell_1^c = \exp(-2)$ is the critical concentration in the adsorption of a one-component gas of species 1, and the vertex P_+ of the triangle $P_t P_+ P_u$ is at infinity ($P_+ \equiv (\exp(-6), \infty)$).

The graphs of the equilibrium position of oscillator $\xi(\ell_1)$ and the surface coverage $\theta_n(\ell_1)$ in figures 4 and 5, respectively, clearly illustrate their essential dependence on the value of S_0 . In the most interesting range $S_0 \in (S_-^c, S_1^c)$ (figures 4(b)–(h) and 5(b)–(h)), these characteristics are shown only in a small interval of ℓ_1 in which the adsorption isotherms essentially differ from the classical Langmuir ones.

For $S_0 < S_-^c$, the coordinate ξ increases with the concentration ℓ_1 and tends to its asymptotic value ξ^a determined from equation (25) (figure 4(a)). According to the analysis in section 3.1, $\xi^a \in (1, 2)$; the numerical analysis shows that ξ^a increases with S_0 . The adsorption isotherms in figure 5(a) are similar to the classical Langmuir isotherms. However, unlike the Langmuir case for which the ratio θ_2/θ_1 is the constant equal to S_0 , variations in the adsorption properties of the adsorbent in the competitive adsorption lead to the dependence of this ratio on the concentration ℓ_1 . As ℓ_1 increases, the ratio θ_2/θ_1 increases and considerably exceeds the Langmuir one (for large values of ℓ_1 , approximately by a factor of 50).

For $S_0 \in (S_-^c, S_+^c)$, the coordinate $\xi(\ell_1)$ (figure 4(b)) and the surface coverage $\theta_n(\ell_1)$ (figure 5(b)) have a hysteresis in the first bistability interval of the system.

As the concentration ℓ_1 increases from zero, both the coordinate ξ and the surface coverages θ_n increase along their lower stable branches ending at the bifurcation concentration $\ell_1 = \ell_{1,2}^{\rm b}$. At this concentration, ξ and θ_n jump up to their upper stable branches solely due to a change in adsorption properties of the adsorbent. For convenience, transitions between stable branches of $\xi(\ell_1)$ are shown in figure 4 by light vertical straight lines with arrows indicating the direction of transition. Arrows under and above the stable branches of $\xi(\ell_1)$ indicate the direction of variation in ℓ_1 . Furthermore, as the concentration ℓ_1 increases from $\ell_{1,2}^{\rm b}$, the coordinate ξ and the surface coverages θ_n increase along the upper stable branches and tend to their asymptotic values $\xi^{\rm a}$ and $\theta_n^{\rm a}$.



Figure 4. Equilibrium position of oscillator ξ versus the concentration ℓ_1 for different values of S_0 : $S_0 = 0.003$ (a), 0.0055 (b), S_u (c), 0.005 77 (d), S_d (e), 0.005 85 (f), S_t (g), 0.005 93 (h), 0.01 (i); $G = 2, g_1 = 3.5$.

The transition of the coordinate ξ from the lower stable branch to the upper one at the bifurcation concentration $\ell_{1,2}^{b}$ is accompanied by an increase in the activation energy for desorption of adparticles, which hampers their desorption. As a result, as the concentration ℓ_1 decreases from a value greater than $\ell_{1,2}^{b}$, the reverse transition of ξ and θ_n from their upper stable branches to the lower ones occurs at the lower bifurcation concentration $\ell_{1,1}^{b} < \ell_{1,2}^{b}$.

The curves in figures 4(c) and 5(c) correspond to the special case $S_0 = S_u$ where the system has two bistability intervals with a common point $\ell_1 = \ell_u^b$. Each of the functions $\xi(\ell_1)$ and $\theta_n(\ell_1)$ has three stable and two unstable branches (the *j*th unstable branch connects the *j*th and (j + 1)th stable branches, where j = 1, 2). However, the behaviors of these functions are different. The coordinate $\xi(\ell_1)$ has two successive hystereses in the touching bistability intervals (figure 4(c)). As the concentration ℓ_1 increases from zero, the coordinate ξ increases along the first stable branch up to its end at $\ell_1 = \ell_u^b$, then jumps up to the second stable branch and

increases with ℓ_1 along this branch up to its end at $\ell_1 = \ell_{1,4}^b$, then jumps up to the third stable branch and increases along it, tending to its asymptotic value ξ^a . As the concentration ℓ_1 decreases from a value greater than $\ell_{1,4}^b$, the coordinate ξ successively jumps down from the third stable branch to the second and from the second stable branch to the first one at the bifurcation concentrations ℓ_u^b and $\ell_{1,1}^b$, respectively, at which these branches end; furthermore, the transitions from the first and third stable branches to the second go along the same vertical straight line $\ell_1 = \ell_u^b$.

The behavior of the surface coverage $\theta_2(\ell_1)$ in figure 5(c) is similar to the behavior of the coordinate $\xi(\ell_1)$ in figure 4(c). Note that a similar behavior of $\theta_2(\ell_1)$ and $\xi(\ell_1)$ also occurs for other values of S_0 (cf curve 2 in figures 5(c)–(i) with the curve in figures 4(c)–(i)).

The surface coverage $\theta_1(\ell_1)$ has another behavior (see curve 1 in figure 5(c)). The different location of the second and third stable branches of $\theta_1(\ell_1)$ and $\theta_2(\ell_1)$ illustrates the essentially different behavior of the surface coverages θ_1



Figure 5. Surface coverages θ_n by adparticles of species n (n = 1, curve 1; n = 2, curve 2) versus the concentration ℓ_1 . The values of S_0 , G and g_1 are the same as in figure 4.

and θ_2 in transition between stable branches at bifurcation concentrations of ℓ_1 . The transition of the surface coverages θ_n from the first stable branch to the second leads to their stepwise increase. However, in transition of the surface coverages θ_n from the second stable branch to the third, the value of θ_2 increases stepwise, whereas the value of θ_1 decreases stepwise. Thus, as the concentration ℓ_1 increases, the surface coverage θ_2 continuously increases with ℓ_1 along its stable branches and increases stepwise in transition between stable branches at a bifurcation concentration of ℓ_1 , whereas the surface coverage θ_1 can continuously both increase and decrease with ℓ_1 along its stable branches and both increase and decrease stepwise in transition between stable branches at a bifurcation concentration of ℓ_1 . This different behavior of $\theta_1(\ell_1)$ and $\theta_2(\ell_1)$ is caused by the different growth of the residence times of adparticles of different species on the deformable adsorbent in adsorption and, furthermore, quantity (14) characterizing this difference exponentially increases with displacement of adsorption sites from their nonperturbed equilibrium position. This leads to a greater amount of adparticles of species 2 relative to that of species 1 (cf the third stable branches of $\theta_1(\ell_1)$ and $\theta_2(\ell_1)$), whereas, in the classical case, $\theta_2 \ll \theta_1$. This result agrees with condition (28), according to which, for $\xi^a > 1.5$, the asymptotic ratio $S(\xi^a)$ defined by relation (27) is greater than 1. Indeed, in the considered case, $\xi^a \approx 1.65$, which yields $S(\xi^a) \approx 1.85$.

One more specific feature is a self-tangency point of $\theta_1(\ell_1)$ (the point of contact of four branches of the function: two stable (first and third) and two unstable branches) at $\ell_1 = \ell_u^b$. As was discussed above, in this special case, there are three stationary coordinates: two two-fold $(\xi_2^b \text{ and } \xi_3^b, \xi_2^b < \xi_3^b)$ and one stable lying between them and equal to the ordinate of the point of intersection of the second stable branch of $\xi(\ell_1)$ with the vertical straight line $\ell_1 = \ell_u^b$ (figure 4(c)). By taking into account the principle of perfect delay [37, 38] and the condition for transition between stationary solutions of the system (according to which all components $(\xi, \theta_1, \theta_2)$ of a stationary three-component solution simultaneously go from their stable branches at a bifurcation concentration at which these branches end to the other corresponding stable branches), as ℓ_1 increases, a discontinuous transition of θ_1 to the second stable branch occurs at $\ell_1 = \ell_u^b$ rather than a continuous transition to the third stable branch touching with the first stable branch at $\ell_1 = \ell_u^b$. Furthermore, as ℓ_1 increases, the surface coverage θ_1 decreases along the second stable branch up to its end at $\ell_1 = \ell_{1,4}^b$, then jumps down to the third stable branch and decreases along this branch tending to its asymptotic value θ_1^a . As the concentration ℓ_1 decreases from a value greater than $\ell_{1,4}^b$, the surface coverage θ_1 varies along the third stable branch up to its end at $\ell_1 = \ell_u^b$, then jumps up to the second stable branch (furthermore, along the same vertical straight line as for increasing ℓ_1 , rather than continuously going to the first stable branch touching the third stable branch at $\ell_1 = \ell_u^b$), then varies along the second stable branch touching the third stable branch at $\ell_1 = \ell_u^b$.

It turns out that the equality of the two bifurcation values of the surface coverage θ_1 for $\ell_1 = \ell_u^b$ and $S_0 = S_u$ ($\theta_{1,2}^b = \theta_{1,3}^b \equiv \theta_1^u$) shown in figure 5(c) also occurs for other values of the parameters g_1 and G; the values of ℓ_u^b and S_u depend on g_1 and G. By using (50) and (48), we obtain that, in this case, the bifurcation coordinates ξ_2^b and ξ_3^b are symmetrically located about G/2: $\xi_2^b = G/2 - \eta$ and $\xi_3^b = G/2 + \eta$. For G = 2, the quantity η is a positive solution of the equation

$$\frac{g_1 x}{1 + g_1 x^2} = \tanh g_1 x \tag{58}$$

the quantities S_u and ℓ_u^b are expressed in terms of η as follows:

$$S_{u} = \frac{\cosh g_{1}\eta}{\cosh 2g_{1}\eta} \frac{\eta \left(1 - \eta \tanh g_{1}\eta\right)}{\left(1 + \eta^{2}\right) \tanh 2g_{1}\eta - 2\eta} \exp\left(-g_{1}\right),$$

$$\ell_{u}^{b} = 2\frac{g_{1}(1 - \eta^{2}) - 1}{1 + g_{1}\eta(1 + \eta)} \exp\left(g_{1}(\eta - 1)\right),$$
(59)

and the bifurcation surface coverages have the form

$$\theta_{1}^{u} = 1 - \eta^{2} - \frac{1}{g_{1}}, \quad \theta_{2,2}^{b} = \frac{1}{2} \left\{ \frac{1}{g_{1}} + \eta (\eta - 1) \right\},$$

$$\theta_{2,3}^{b} = \frac{1}{2} \left\{ \frac{1}{g_{1}} + \eta (\eta + 1) \right\}.$$
 (60)

Equation (58) has a nonzero solution η for $g_1 > 3$ and its value increases with g_1 : $\eta \in (0, 1)$ for $g_1 \in (3, \infty)$. According to (60), as g_1 increases, the difference $\delta^u = \theta_1^u - \theta_{2,3}^b$ decreases from its maximum value $\lim_{g_1\to 3} \delta^u = 0.5$ to the minimum value $\lim_{g_1\to\infty} \delta^u = -1$. For example, $\delta^u \approx 0.453$ for $g_1 = 3.01$ and $\delta^u \approx -0.774$ for $g_1 = 10$. For $g_1 = 3.5$ (figures 4(c) and 5(c)), $\eta \approx 0.468$ and the values of θ_1^u and $\theta_{2,3}^b$ are close to each other ($\delta^u \approx 0.01$).

The curves in figures 4(d)–(h) and 5(d)–(h) correspond to different cases of tristability of the system: partial (figures 4(d), (h) and 5(d), (h)) and complete (figures 4(e)–(g) and 5(e)–(g)) overlapping of the bistability intervals $[\ell_{1,1}^b, \ell_{1,2}^b]$ and $[\ell_{1,3}^b, \ell_{1,4}^b]$. In the domain $\ell_1 \in [\ell_{1,1}^t, \ell_{1,2}^t]$, the coordinate $\xi(\ell_1)$ and the surface coverage $\theta_2(\ell_1)$ have two 'parallel' hystereses.

As the concentration ℓ_1 increases/decreases, the behavior of $\xi(\ell_1)$ in figure 4(d) is similar to the behavior of this function in figure 4(c) but the transitions of ξ from the second (as ℓ_1 increases) and third (as ℓ_1 decreases) stable branches to the second stable branch go along the different vertical straight lines $\ell_1 = \ell_{1,2}^{\rm b}$ and $\ell_1 = \ell_{1,3}^{\rm b}$ rather than the same one as in figure 4(c).

The behavior of $\theta_1(\ell_1)$ in figure 5(d) is similar to its behavior in figure 5(c) but with the replacement of the self-tangency point of $\theta_1(\ell_1)$ in figure 5(c) by two self-intersection points of $\theta_1(\ell_1)$ in figure 5(d), one of which is the point of intersection of the first and third stable branches and the second is the point of intersection of the unstable branches. Note that the intersection of two stable branches of $\theta_1(\ell_1)$ means only the same value of θ_1 for two different displacements of adsorption sites ξ for the corresponding value of ℓ_1 , i.e. a partial degeneration of two stationary three-component (θ_1 in this case) rather than a continuous transition between stable branches of $\theta_1(\ell_1)$ at the point of their intersection, which is forbidden by the condition for transition between stationary solutions of the system.

In the special case $S_0 = S_d$ where system (7) has two two-fold stationary solutions, the behavior of $\xi(\ell_1)$ and $\theta_n(\ell_1)$ in figures 4(e) and 5(e) is similar to their behavior in figures 4(d) and 5(d) only for increasing ℓ_1 . As the concentration ℓ_1 decreases from a value greater than $\ell_{1,4}^b$, these quantities vary along their third stable branches up to their end at $\ell_1 = \ell_d^b$; then ξ and θ_2 successively jump down, first, to the second stable branches and then to the first stable branches, whereas θ_1 successively, first, jumps up to the second stable branch and then jumps down to the first stable branch. Then ξ and θ_n decrease along their first stable branches.

The curves in figures 4(f) and 5(f) distinctly illustrate discontinuous transitions of ξ and θ_n from the third stable branches directly to the first stable branches at $\ell_1 = \ell_{1,3}^{\rm b}$ for $S_0 \in (S_d, S_t)$ as the concentration ℓ_1 decreases, which implies that a stationary solution of system (7) on the second stationary branch can be achieved only for increasing ℓ_1 .

In the special case $S_0 = S_t$ where system (7) has two two-fold stationary solutions (figures 4(g) and 5(g)), as the concentration ℓ_1 increases from zero, ξ and θ_n increase along their first stable branches up to their end at $\ell_1 = \ell_t^b$. At this bifurcation concentration, ξ and θ_2 successively jump up, first, to their second stable branches and then to the third stable branches, whereas θ_1 , first, jumps up to the second stable branch and then jumps down to the third stable branch. Then ξ and θ_n vary along their third stable branches. As the concentration ℓ_1 decreases from a value greater than ℓ_t^b , the behavior of $\xi(\ell_1)$ and $\theta_n(\ell_1)$ ('disregard' of the second stable branches) is similar to their behavior in figures 4(f) and 5(f).

The curves in figures 4(h) and 5(h) for $S_0 \in (S_t, S_1^c)$ illustrate that $\xi(\ell_1)$ and $\theta_n(\ell_1)$ 'disregard' the second stationary branches both for increasing (from a value less than $\ell_{1,1}^b$) and decreasing (from a value greater than ℓ_t^b) concentration ℓ_1 . Thus, a stationary solution of system (7) on the second stable branch cannot be achieved by transition from any other stable branch and, hence, a tristable system behaves like a bistable one.

As is seen in figures 4(c)–(h) and 5(c)–(h), the length of the second stable branch decreases as $S_0 \in [S_u, S_1^c]$ increases (most clearly, it is illustrated by the second stable branch of



Figure 6. Equilibrium position of oscillator ξ versus the concentration ℓ_1 for different values of S_0 : $S_0 = 0.0003$ (a), 0.000 475 (b), 0.000 48 (c), 0.000 55 (d), 0.000 66 (f); $G = 2, g_1 = 5$.

 $\theta_1(\ell_1)$) and becomes equal to zero for $S_0 = S_1^c$, which leads to the union of two unstable branches.

For $S_0 > S_1^c$, the coordinate $\xi(\ell_1)$ (figure 4(i)) and the surface coverage $\theta_2(\ell_1)$ (figure 5(i)) have a single hysteresis in the domain $\ell \in [\ell_{1,3}^b, \ell_{1,2}^b]$, whereas the surface coverage $\theta_1(\ell_1)$ has a loop: two intersecting stable branches connected by the unstable branch (figure 5(i)). Transitions between the stable branches of $\theta_1(\ell_1)$ are discontinuous at $\ell = \ell_{1,2}^b$ (as ℓ_1 increases) and $\ell = \ell_{1,3}^b$ (as ℓ_1 decreases) rather than a continuous transition at the point of their intersection.

The curves in figure 5(i) illustrate that the asymptotical value θ_2^a of the surface coverage θ_2 considerably exceeds the asymptotical value θ_1^a of the surface coverage θ_1 ($S(\xi^a) \approx 7.12$). Thus, due to a great displacement of adsorption sites ($\xi^a \approx 1.88$), the adsorbent surface is occupied mainly by adparticles of species 2 rather than adparticles of species 1 as in the Langmuir case.

3.5. Adsorption isotherms with several asymptotes

As has been shown in section 3.1, the coordinate $\xi(\ell_1)$ and the surface coverages $\theta_n(\ell_1)$ have three horizontal asymptotes (two stable and one unstable) if $g_1 > g_c^a$ and, for example, $S_0 \in (S_-^a, S_+^a)$ for G > 1. For G = 2, $g_c^a = g_c = 4$ and $S_c^a = \exp(-6) \approx 0.00248$.

The graphs of $\xi(\ell_1)$ and $\theta_n(\ell_1)$ for $g_1 = 5$ depicted in figures 6 and 7, respectively, illustrate specific features of these functions in the case where a stationary solution of system (7) has several asymptotes. In this case, $S_{-}^a \approx$ 0.000 4734 and $S_{+}^a \approx 0.000$ 6462.

For $S_0 < S_-^a$, the coordinate $\xi(\ell_1)$ (figure 6(a)) and the surface coverages $\theta_n(\ell_1)$ (figure 7(a)) have a hysteresis typical

of these quantities in adsorption of a one-component gas for values of the coupling parameter greater than critical [27] or a two-component gas; for example, for $g_1 \in (3, 4)$ and $S_0 \in (S_-^c, S_+^c)$ (see figures 4(b) and 5(b)). The coordinate $\xi(\ell_1)$ consists of three branches: two stable branches (the lower stable branch for $\ell_1 \in [0, \ell_{1,2}^b]$ and the upper stable branch for $\ell_1 \in [\ell_{1,1}^b, \infty)$ that approaches its horizontal asymptote $\xi = \xi_1^a$ as ℓ_1 increases) and one unstable branch connecting them. The surface coverages $\theta_n(\ell_1)$ have a similar shape. For all considered values of S_0 , the lower stable branch of $\theta_2(\ell_1)$ in figure 7 almost coincides with the abscissa axis.

For $S_0 \in (S_-^a, S_+^a)$, the behavior of $\xi(\ell_1)$ and $\theta_n(\ell_1)$ qualitatively differs from their behavior in figures 4 and 5. For $S_0 > S_-^a$, there appears an isolated piece of $\xi(\ell_1)$ with a semi-infinite domain of definition $\ell_1 \in [\ell_{1,3}^b, \infty)$ (figure 6(b)). This isolated piece consists of stable and unstable branches starting at the bifurcation concentration $\ell_{1,3}^{b}$ and rapidly tending to closely lying asymptotes $\xi = \xi_3^a$ and $\xi = \xi_2^a$ ($\xi_3^a >$ ξ_2^a), respectively, as ℓ_1 increases. Thus, the range of values of the positive-definite function $\xi(\ell_1)$ consists of two intervals $(\xi \in [0, \xi_1^a) \text{ and } \xi \in (\xi_2^a, \xi_3^a))$ with a gap $\xi \in (\xi_1^a, \xi_2^a)$ between them. According to the principle of perfect delay [37, 38], the transition from the first piece ($\xi \in [0, \xi_1^a)$) of $\xi(\ell_1)$ to the isolated piece ($\xi \in (\xi_2^a, \xi_3^a)$) with variation in ℓ_1 is impossible for any initial value of ℓ_1 . If the initial state of the system lies on the stable branch of the isolated piece of $\xi(\ell_1)$, then, as the concentration ℓ_1 decreases, the coordinate ξ varies along this branch up to its end at $\ell_1 = \ell_{1,3}^b$, then jumps down to the upper stable branch of the first piece of $\xi(\ell_1)$ and varies along it in the same way as in figure 6(a).

Since the behavior of the surface coverage $\theta_2(\ell_1)$ in figure 7(b) is similar to the behavior of the coordinate $\xi(\ell_1)$



Figure 7. Surface coverages θ_n by adparticles of species n (n = 1, curve 1; n = 2, curve 2) versus the concentration ℓ_1 . The values of S_0 , G and g_1 are the same as in figure 6.

in figure 6(b), all conclusions for $\xi(\ell_1)$ remain true for $\theta_2(\ell_1)$. Moreover, this also holds for other values of S_0 (cf curve 2 in figures 7(c)–(f) with the curve in figures 6(c)–(f)).

The surface coverage $\theta_1(\ell_1)$ in figure 7(b) also has the isolated piece. However, unlike the isolated pieces of $\theta_2(\ell_1)$ and $\xi(\ell_1)$ (figure 6(b)), it lies below the asymptote $\theta_1 = \theta_{1,1}^a$ of the first piece of $\theta_1(\ell_1)$, $\theta_{1,1}^a > \theta_{1,2}^a > \theta_{1,3}^a$. As $S_0 \in (S_-^a, S_+^a)$ increases, the isolated piece of $\xi(\ell_1)$

As $S_0 \in (S_-^a, S_+^a)$ increases, the isolated piece of $\xi(\ell_1)$ shifts to the ordinate axis (the bifurcation concentration $\ell_{1,3}^b$ decreases), its thickness increases, and, at a certain interval of ℓ_1 , the system is tristable (figures 6(c)–(e)). As above, the transition from the first piece of $\xi(\ell_1)$ to the isolated piece with variation in ℓ_1 is impossible. However, as the concentration ℓ_1 decreases, the transition from the stable branch of the isolated piece of $\xi(\ell_1)$ to the lower stable branch (rather than the upper stable branch as in figure 6(b)) of the first piece of $\xi(\ell_1)$ occurs at $\ell_1 = \ell_{1,3}^b$.

Unlike the surface coverage $\theta_2(\ell_1)$, the pieces of the surface coverage $\theta_1(\ell_1)$ in figures 7(c)–(e) intersect one another. However, the continuous transition between stable branches of the different pieces of $\theta_1(\ell_1)$ at the point of their intersection is forbidden by the condition for transition between stationary solutions of the system.

For $S_0 > S_{+}^a$, the gap between two pieces of $\xi(\ell_1)$ disappears $(\ell_{1,4}^b$ is finite) and the function $\xi(\ell_1)$ is continuous and has three stable and two unstable branches (figure 6(f)). There are two bistability intervals $(\ell_{1,3}^b, \ell_{1,1}^b)$ and $(\ell_{1,2}^b, \ell_{1,4}^b)$ and one tristability interval $(\ell_{1,1}^b, \ell_{1,2}^b)$ between them. The graph of $\theta_1(\ell_1)$ in figure 7(f) is also continuous and consists of three stable branches and two unstable branches connecting them. However, the shapes of $\theta_1(\ell_1)$ and $\theta_2(\ell_1)$ are essentially different. For $\ell_1 > \ell_{1,4}^b$, the adsorption sites are considerably

displaced from their nonperturbed equilibrium position $\xi = 0$ so that $\xi(\ell_1)$ is, in fact, a constant (figure 6(f)). In this case, an almost monolayer coverage of the surface mainly by adparticles of species 2 occurs (cf the flat regions of the curves in figure 7(f)), whereas, in the classical case, the surface coverage by adparticles of species 2 is less than 0.1% of the total coverage.

4. Adiabatic approximation

The specific features of stationary solutions of system (7) investigated in section 3 can be explained with the use of a potential. To this end, we consider the last equation of system (7) in the overdamped approximation where the masses of an adsorption site and adparticles are low and the friction coefficient is so large that the first term on the left-hand side of this equation can be neglected compared to the second. By using the well-known results for a linear free oscillator of constant mass [39], this approximation is correct if

$$\tau_M^2 \ll \tau_r^2,\tag{61}$$

where $\tau_M = 1/\omega_M$, $\omega_M = \sqrt{\varkappa/M}$ is the vibration frequency of an oscillator of mass *M*, and $\tau_r = \alpha/\varkappa$ is the typical relaxation time of a massless oscillator.

Furthermore, we consider the case where the relaxation time of the coordinate $\xi(t)$ of a massless oscillator is much greater than the relaxation times of the surface coverages $\theta_n(t)$, n = 1, 2, in the linear case; i.e. the variables ξ and θ_n are slow and fast, respectively. In this case, $\tau_r \gg \tau_{\theta}$, where

$$\tau_{\theta} \approx 2 \left\{ \left(\frac{1}{\tau_1^{ad}} + \frac{1}{\tau_2^{ad}} \right) - \sqrt{\left(\frac{1}{\tau_1^{ad}} - \frac{1}{\tau_2^{ad}} \right)^2 + \frac{4}{\tau_1^a \tau_2^a}} \right\}^{-1}$$
(62)



Figure 8. Normalized potential for G = 2, $g_1 = 3.5$, $S_0 = 0.0055$, and different values of the concentration ℓ_1 : $\ell_1 = 0.158$ (1), 0.158 26 (2), 0.1585 (3) (a); $\ell_{1,1}^{b}$ (1), 0.1582 (2), $\ell_{1,2}^{b}$ (3) (b).

 $\tau_n^{ad} = \tau_n^a \tau_n^d / (\tau_n^a + \tau_n^d)$ is the time taken for the surface coverage θ_n to reach the stationary value in the case of the Langmuir adsorption of a one-component gas of species *n*, and $\tau_n^a = 1/k_n^a C_n$ can be regarded as the typical lifetime of a vacant adsorption site in this case. By using the principle of adiabatic elimination of the fast variables $\theta_n(t)$ in (7) [40], we set $d\theta_n/dt = 0$, n = 1, 2, and express the surface coverage θ_1 versus the slow variable ξ as follows:

$$\theta_1 = \frac{\ell_1}{\ell_1 \left(1 + S(\xi)\right) + \exp(-g_1 \xi)}.$$
(63)

The surface coverage θ_2 is defined by relation (17) with θ_1 given by relation (63). The coordinate $\xi(t)$ is determined as a solution of the nonlinear differential equation

$$\alpha \frac{\mathrm{d}\xi}{\mathrm{d}t} = -\frac{\mathrm{d}U(\xi)}{\mathrm{d}\xi} \tag{64}$$

that describes the motion of a massless oscillator in the potential

$$U(\xi) = \frac{\kappa}{2} \left\{ \xi^2 - 2h(\xi) \right\},$$
 (65)

where the second term on the right-hand side of (65) caused by the adsorption-induced force acting on an adsorption site has the form

$$h(\xi) = \ell_1 \int_0^{\xi} dy \, \frac{1 + G \, S(y)}{\ell_1 \, (1 + S(y)) + \exp(-g_1 \, y)}.$$
 (66)

Relations (17), (63) and (64) correctly describe the behavior of the dynamical variables $\xi(t)$ and $\theta_n(t)$ for times $t \gg \tau_{\theta}$, for which the fast variables $\theta_n(t)$ forget the initial data.

The shape of $U(\xi)$ essentially depends on the control parameters ℓ_1 , g_1 , S_0 and G. The stationary solutions ξ_k of equation (64), where the subscript k is the number of a stationary solution, are roots of equation (18) and, furthermore, the number of roots can vary from 1 to 5 depending on the values of the control parameters. The roots are enumerated so that $\xi_{k+1} > \xi_k$, and $U_k \equiv U(\xi_k)$. For simple roots, the odd and even values of k correspond to the stable (minima of $U(\xi)$) and unstable (maxima of $U(\xi)$) stationary solutions of equation (64), respectively. For a double root ξ_k , the potential has a point of inflection at $\xi = \xi_k$ and equation (64) has a two-fold stationary solution.

In the special case G = 1, relation (65) is reduced to the potential in adsorption of a one-component gas on a deformable adsorbent [27] with ℓ replaced by ℓ_+

$$U(\xi) = \frac{\kappa}{2} \left\{ \xi^2 - 2\xi - \frac{2}{g} \ln \frac{\ell_+ + \exp\left(-g\xi\right)}{\ell_+ + 1} \right\}.$$
 (67)

By using the results for one-component adsorption [27], we conclude that, for g > 4 and $\ell_+ \in (\ell_{+,1}^b, \ell_{+,2}^b)$, $U(\xi)$ is a two-well potential with local minima at $\xi = \xi_1$ and ξ_3 separated by a maximum at $\xi = \xi_2$, where ξ_k , k = 1, 2, 3, are the coordinates determined from equation (36) with regard to relation (35). Thus, the system under study is bistable. For g < 4 and any concentrations ℓ_1 and ℓ_2 as well as for g > 4and $\ell_+ \notin [\ell_{+,1}^b, \ell_{+,2}^b]$, the potential $U(\xi)$ has one minimum and, hence, the considered system is monostable.

Note that for $\ell_{+} = \ell_{+}^{M}$, where $\ell_{+}^{M} = \exp(-g/2)$, potential (67) is an even function about $\xi = 1/2$. Hence, in this case, $U(\xi)$ is either a single-well potential with minimum at $\xi = 1/2$ equal to $U^{M} \equiv U(1/2) =$ $(\varkappa/8) \{(8/g) \ln \cosh(g/4) - 1\}$ if $g \leq 4$ or, for g > 4, a symmetric two-well potential with maximum value U^{M} at $\xi = 1/2$ and two equal minima at $\xi = \xi_{+}^{M}$ and ξ_{-}^{M} , where $\xi_{\pm}^{M} = 1/2 \pm (2/g) \eta$ and η is a positive solution of the equation

$$\frac{4x}{g} = \tanh x. \tag{68}$$

Following [37, 38], for g > 4, the quantity ℓ_+^M may be called a Maxwell concentration.

In another special case G = 0, the potential $U(\xi)$ is also defined by relation (67) with ℓ_+ replaced by $\ell_1/(1 + \ell_2)$.

In what follows, we analyze the potential $U(\xi)$ in the case G = 2, for which the coordinate $\xi(\ell_1)$ and the surface coverages $\theta_n(\ell_1)$ have been investigated in sections 3.4 and 3.5

For $g_1 \in (3, 4)$, $U(\xi)$ is a single-well potential if $S_0 < S_-^c$. For the given values of g_1 and S_0 , the depth of the well $|U_1|$ and the position of its minimum ξ_1 increase with ℓ_1 . As S_0 increases, for $S_0 > S_-^c$, the situation cardinally changes and, for the given value of g_1 , the shape of the potential essentially depends on the values of ℓ_1 and S_0 . If $S_0 \in (S_-^c, S_+^c)$, then



Figure 9. Normalized potential for G = 2, $g_1 = 3.5$, $S_0 = 0.005$ 85, and different values of the concentration ℓ_1 : $\ell_1 = \ell_{1,1}^{b}$ (1), 0.155 (2) (a); 0.1558 (1), 0.156 (2), 0.157 (3) (b); $\ell_{1,2}^{b}$ (1), 0.159 (2), $\ell_{1,4}^{b}$ (3) (c).

the potential has either two minima if $\ell_1 \in (\ell_{1,1}^b, \ell_{1,2}^b)$ or one minimum if $\ell_1 \notin [\ell_{1,1}^b, \ell_{1,2}^b]$.

For $S_0 = 0.0055 \in (S_-^c, S_+^c)$, the curves in figure 8(a) illustrate the two-well shape of the potential for $\ell_1 \in$ $(\ell_{1,1}^{b}, \ell_{1,2}^{b})$, where $\ell_{1,1}^{b} \approx 0.1575$ and $\ell_{1,2}^{b} \approx 0.159$. The curves in figure 8(b) show essential changes in the shape of the potential for the bifurcation concentrations $\ell_{1,1}^{b}$ (curve 1) and $\ell_{1,2}^{b}$ (curve 3); namely, as ℓ_1 increases, the single-well potential for $\ell_1 < \ell_{1,1}^{b}$ is transformed into a two-well potential for $\ell_1 > \ell_{1,1}^b$, and then the two-well potential for $\ell_1 \in$ $(\ell_{1,1}^{b}, \ell_{1,2}^{b})$ is transformed into a single-well potential for $\ell_{1} >$ $\ell_1^{\rm b}$ 2. Curve 1 in figure 8(a) shows the appearance of the second stationary (metastable because $U_1 < U_3$) state of the system at the greater displacement ξ_3 ($\xi_3 > \xi_1$) of the oscillator from its nonperturbed equilibrium position $\xi = 0$. An increase in ℓ_1 is accompanied by an increase in the depths of both wells and a decrease in the barrier $\delta_{2,1} = U_2 - U_1$ between the wells. Since the increment of the depth of the second well with ℓ_1 is greater than that of the first well, for some value of ℓ_1 (called a Maxwell concentration), the wells have equal depths (curve 2 in figure 8(a)) and, for greater values of ℓ_1 , the second well is deeper than the first (curve 3 in figure 8(a)), i.e. the state of the system becomes metastable in the first well and stable in the second. Nevertheless, within the framework of the overdamped approximation, following the principle of perfect delay [37, 38], as ℓ_1 increases, the oscillator remains in the first well rather than moving to the second. For the transition of the system from the metastable state to the stable state according to the Maxwell principle of the choice of the global minimum of the potential [37, 38], thermal fluctuations or the inertia effect (as in [41] in the case of one-component adsorption) or both these factors should be taken into account. This situation remains up to the bifurcation concentration $\ell_{1,2}^{b}$ for which the barrier $\delta_{2,1} = 0$ (curve 3 in figure 8(b)). A negligible excess of this bifurcation concentration leads to the transformation of $U(\xi)$ into a single-well potential, which is accompanied by the displacement of the oscillator to the unique equilibrium position at the point ξ_3 or, in terms of $\xi(\ell_1)$, the transition of the coordinate $\xi(\ell_1)$ from its lower stable branch to the upper one at $\ell_1 = \ell_{1,2}^{b}$ (see figure 4(b)). In turn, this is accompanied by transitions of the surface



Figure 10. Normalized potential for $\ell_1 = \infty$, G = 2, $g_1 = 5$, and different values of S_0 : $S_0 = 0.0004$ (1), 0.0005 (2), S_0^M (3), 0.0006 (4), 0.0007 (5).

coverages $\theta_n(\ell_1)$ from their lower stable branches to the upper ones (figure 5(b)).

The curves in figure 9 for $S_0 = 0.005\,85 \in (S_d, S_t)$ illustrate the transformation of the two-well potential $U(\xi)$ for $\ell_1 < \ell_{1,1}^{b} \approx 0.154$ into a three-well potential, and vice versa for $\ell_1 > \ell_{1,2}^b \approx 0.158$ as ℓ_1 increases. For the bifurcation concentration $\ell_{1,1}^{b}$, the potential has two wells and a point of inflection between them (curve 1 in figure 9(a)). As ℓ_1 increases, the potential is deformed in the neighborhood of this point of inflection so that there appears one more well (curve 2 in figure 9(a)). The depths of the wells at $\xi = \xi_k$, where k = 1, 3, 5, decrease with ξ : $|U_1| > |U_3| >$ $|U_5|$. As ℓ_1 increases, this inequality is replaced, first, by $|U_1| > |U_5| > |U_3|$ (curve 1 in figure 9(b)) and then by $|U_5| > |U_3| > |U_1|$ (curves 2 and 3 in figure 9(b)), i.e. the deepest well successively moves away from the nonperturbed equilibrium position $\xi = 0$ as ℓ_1 increases. For the bifurcation concentration $\ell^{b}_{1,2}$ the barrier between the first and second wells disappears, $\delta_{2,1} = 0$ (curve 1 in figure 9(c)). A negligible excess of this bifurcation concentration leads to the transformation of $U(\xi)$ into a two-well potential and, as a result, the displacement of the oscillator to the equilibrium position at the point ξ_3 or, in terms of $\xi(\ell_1)$, the transition



Figure 11. Normalized potential for G = 2, $g_1 = 5$, the concentration $\ell_1 = 10$ (1), 20 (2), ∞ (3), and $S_0 = 0.0005$ (a), $S_0^{(1)}$ (b), 0.0006 (c).

of the coordinate $\xi(\ell_1)$ from its first stable branch to the second at $\ell_1 = \ell_{1,2}^b$ (figure 4(f)). In turn, this is accompanied by transitions of the surface coverages $\theta_n(\ell_1)$ from their first stable branches to the second (figure 5(f)). As ℓ_1 increases, the two-well potential is transformed so that the barrier between the two remaining wells $\delta_{4,3} = U_4 - U_3$ decreases and becomes equal to zero for the bifurcation concentration $\ell_{1,4}^b \approx 0.161$ (curve 3 in figure 9(c)). For $\ell_1 > \ell_{1,4}^b$, only one well of the potential $U(\xi)$ most remote from the nonperturbed surface remains and the oscillator shifts to the bottom of this well at $\xi = \xi_5$.

By taking into account the different increase in the residence times of adparticles of different species on the surface with displacement of adsorption sites from the nonperturbed adsorbent surface (see (9)–(14)), we can draw the conclusion that there is a considerable increase in the fraction of adparticles of species 2 in the total amount of adsorbed substance in the transition of adsorption sites to a more remote well. This conclusion explains, in particular, the opposite behavior of the surface coverages $\theta_1(\ell_1)$ and $\theta_2(\ell_1)$ in figures 5(c)–(f) and (i) in passing through the bifurcation value $\ell_{1,4}^{b}$: the stepwise decrease in $\theta_1(\ell_1)$ and the stepwise increase in $\theta_2(\ell_1)$ are caused by the displacement of the adsorption sites to the most remote well.

As has been shown in section 3.1, the specific feature of adsorption of a two-component gas on a deformable adsorbent is two stable horizontal asymptotes of the coordinate $\xi(\ell_1)$ and the surface coverages $\theta_n(\ell_1)$ for some values of control parameters. To explain this effect in terms of the potential $U(\xi)$, we investigate its behavior in the limiting case of infinitely large values of ℓ_1 . By passing in (66) to the limit $\ell_1 \rightarrow \infty$, we obtain

$$U^{a}(\xi) \equiv \lim_{\ell_{1} \to \infty} U(\xi) = \frac{\kappa}{2} \left\{ \xi^{2} - 2\xi - \frac{2}{g_{1}} \ln \frac{1 + S(\xi)}{1 + S_{0}} \right\}.$$
(69)

For a finite ℓ_2 , $S_0 = 0$ and relation (69) is reduced to the parabolic potential

$$U^{a}(\xi) = \varkappa \, \xi \left(\frac{\xi}{2} - 1\right) \tag{70}$$

with a minimum at the point $\xi = 1$.

By taking into account that the functions $\xi(\ell_1)$ and $\theta_n(\ell_1)$ have two stable horizontal asymptotes if $g_1 > g_c^a$ and $S_0 \in (S_-^a, S_+^a)$ for G > 1, we conclude that, for these values of

G, g_1 and S_0 , $U^a(\xi)$ is a two-well potential and the system under study is bistable in a semi-infinite interval of values of ℓ_1 .

It is worth noting that for $S_0 = S_0^M$, where $S_0^M = \exp(2\beta q_a)$ and the quantities β and q_a are defined by (29), the potential $U^a(\xi)$ is an even function about $\xi = \xi_c^a = (1+G)/2$. In this case, $U^a(\xi)$ is either a single-well potential with a minimum at $\xi = \xi_c^a$ equal to $U_M^a \equiv U^a(\xi_c^a) = (\varkappa/2) \{\xi_c^a (\xi_c^a - 2) + (2/g_1) \ln ((1+S_0^M)/2))\}$ if $g_1 \leq g_c^a$ or, for $g_1 > g_c^a$, a symmetric two-well potential with maximum value U_M^a at $\xi = \xi_c^a$ and two equal minima at $\xi = \xi_{M+}^a$ and $\xi = \xi_{M-}^a$, where $\xi_{M\pm}^a = \xi_c^a \pm (2/(g_1 (G-1))) \eta$ and η is a positive solution of the equation

$$\frac{x}{q_{\rm a}} = \tanh x. \tag{71}$$

Note that equation (71) with q_a replaced by $g_1/4$ coincides with equation (68). For $g_1 > g_c^a$, the quantity S_0^M may be called a Maxwell value of the parameter S_0 .

The curves in figure 10 clearly illustrate the essential dependence of the potential $U^{a}(\xi)$ on the value of S_{0} . In this case, $\xi_{c}^{a} = 3/2$, $S_{0}^{M} \approx 0.000553$, and $\eta \approx 0.355$. For $S_{0} < S_{-}^{a} \approx 0.000473$ (curve 1) and $S_{0} > S_{+}^{a} \approx 0.000646$ (curve 5), the potential has one well; furthermore, in the second case, the well is deeper and considerably more shifted from the nonperturbed adsorbent surface $\xi = 0$. For $S_{0} \in (S_{-}^{a}, S_{+}^{a})$, the potential has two wells; moreover, the first well is deeper than the second if $S_{0} \in (S_{-}^{a}, S_{0}^{M})$ (curve 2) and the second well is deeper than the first if $S_{0} \in (S_{0}^{M}, S_{+}^{a})$ (curve 4). Curve 3 corresponds to the symmetric two-well potential. The two-well potential $U^{a}(\xi)$ leads to two disconnected pieces of $\xi(\ell_{1})$ (see figures 6(b)–(e)) and the corresponding specific features of $\theta_{1}(\ell_{1})$ and $\theta_{2}(\ell_{1})$ (see figures 7(b)–(e)).

The curves in figure 11 show the approach of the potential $U(\xi)$ to the two-well potential $U^{a}(\xi)$ as ℓ_{1} increases. For large values of ℓ_{1} , the behavior of the two-well potential $U(\xi)$ is similar to $U^{a}(\xi)$: the first well is deeper if $S_{0} \in (S_{-}^{M}, S_{0}^{M})$ (figure 11(a)), the second well is deeper if $S_{0} \in (S_{0}^{M}, S_{+}^{a})$ (figure 11(c)), and, for the Maxwell value S_{0}^{M} of the parameter S_{0} , the depths of two wells are equal (figure 11(b)). Since the first well of the potential does not disappear with an increase in the concentration ℓ_{1} , according to the principle of perfect delay [37, 38], the oscillator, which was in this well at low concentrations, remains in it for arbitrarily large values of ℓ_{1} .

5. Conclusions

In the present paper, we have investigated isotherms of competitive adsorption of a two-component gas on the surface of a solid adsorbent whose adsorption properties vary in adsorption due to the adsorbent deformation. It has been established that taking account of the adsorbent deformation in adsorption essentially changes the shape of adsorption isotherms relative to the Langmuir isotherms. The specific features of adsorption isotherms (bistability and tristability of the system, two stable asymptotes of adsorption isotherms, and an essential redistribution of the quantities of adsorbed particles of different species as compared with those in the classical case) depend on values of the parameters expressed in terms of the phenomenological constant adsorption-induced forces χ_1 and χ_2 . The values of these forces can be determined knowing the experimental data of changes in the first interplanar spacing (along the normal to the surface) x_n^{max} due to the total monolayer coverage of the adsorbent surface by adparticles of species n in the adsorption of a one-component gas. In terms of the measured x_n^{max} , the required forces and the coupling parameters are expressed as follows:

$$\chi_n = \varkappa \, x_n^{\max}, \quad g_n = \varkappa \, (x_n^{\max})^2 / k_{\rm B} T,
n = 1, 2, \quad G = x_2^{\max} / x_1^{\max}.$$
(72)

Given the reliable experimental data for x^{max} for different absorbents and adsorbates and based on the values of the parameters calculated by relations (72), it is possible to indicate adsorbent–adsorbate systems for which the established effects caused by the adsorbent deformation in adsorption occur. According to (72), this is more probable for adsorbents with considerable displacement of adsorption sites in adsorption. Possibly, in experiments aimed at searching for these effects, it makes sense to use single crystal solid substrates of a 'soft' material, admitting a considerable normal displacement of the adsorbent surface in adsorption.

It is also worth noting that the used mean-field approximation requires that the relaxation time of a bound adsorption site to a new equilibrium position caused by adsorption is much greater than the average time between collisions of gas particles with the adsorption site and the average residence time of an adparticle on the surface. For this relaxation time to be much more greater than the vibrational period of a vacant adsorption site, the friction coefficient must not be negligible. This imposes some conditions on its value, which depends on the concentration of particles in the gas phase, so that many gas particles can successively take part in adsorption on the same adsorption site before it reaches the equilibrium position.

The proposed model of competitive adsorption of a two-component gas on a deformable adsorbent should be regarded as only the first step for describing adsorption on a deformable adsorbent. The subsequent development of the model requires taking account of various factors (lateral interactions between adparticles, fluctuations, energy inhomogeneity of the adsorbent surface, etc) not considered here.

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