

DYNAMIC ADSORPTION IN A RADIAL FLOW OF A SOLUTION AROUND A SPHERICAL CAVITY

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The paper studies the local variation of the concentration of a neutral dilute solution during its radial flow around a spherical cavity in the approximations of an adsorption layer and the Langmuir adsorption kinetics. The authors used the boundary-layer method and the method of asymptotic series expansion of the solution in a small parameter, which is the ratio of the time of establishing an adsorption equilibrium to the time of establishing a steady diffusion layer around the cavity. The equations obtained for a zeroth approximation were studied analytically and numerically. In the case of high-frequency oscillations of the cavity in the solution, a solution of the problem was found that corresponds to the process of "straightened" adsorption or "pumping" an admixture into the adsorption layer.

Introduction. It was found experimentally that in some cases the passage of shock waves or the effect of an intense ultrasonic field lead to a considerable decrease in the induction period of solid-phase extraction in oversaturated solutions [1, 2]. This effect is intensified by exciting cavitation in the solution: a large number of bubble–microcrystal pairs is formed [3]. This process has been studied in a number of theoretical papers (see, for example, a review in [3]).

In the present paper, local variation of solution saturation in a radial flow around a spherical cavity simulating a gas bubble is considered as a possible mechanism of decreasing the induction period of solid-phase extraction in oversaturated solutions. The local variation of saturation is due to the disturbance of the adsorption equilibrium of the dissolved admixture in a thin layer on the "solution–cavity" surface in the radial flow around the spherical cavity. Adsorption implies an increase (positive adsorption) or decrease (negative adsorption) in dissolved-component concentration on the interface due to the long-range electromagnetic interaction of admixture molecules with the solvent, which is not compensated for by the cavity. The choice of the cavity as the object of our study is motivated by the necessity of eliminating the effect of thermal processes occurring during expansion, compression, or oscillations of a gas bubble in a liquid.

Nonequilibrium or dynamic adsorption of a gas bubble on the surface has been studied previously in the solution of the classical problem of the effect of surface–active substances (SAS) on gas-bubble motion in the liquid [4, 5]. Recently, several papers have been published on the dynamic adsorption of SAS during growth of a gas bubble in the context of kinetic studies of the formation of volume foam structures (see, for example, [6]). However, in a general formulation (expansion, compression, and cavity pulsations), the problem of dynamic adsorption has not been considered. The solution obtained in the present paper corresponds to the processes of "straightened" adsorption or "pumping" of an admixture into an adsorption layer during high-frequency cavity oscillations in the solution. This problem is of considerable interest for analysis of physicochemical processes in gas–liquid media.

Formulation of the Problem. We consider a spherical cavity of radius R_0 in a dilute solution with a dissolved neutral component S having volume concentration c_0 . The component S is adsorbed on the interface between the solution and the cavity so that its concentration around the spherical cavity changes under the law $c_S = c_S^{(0)}(r)$ ($r \geq R_0$, where r is the modulus of the radius-vector of a spherical coordinate system whose origin

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coincides with the cavity center). As a rule, the characteristic thickness Δ of the adsorption layer on which the function $c_S^{(0)}(r)$ decreases (or increases) rapidly to the value c_0 is of the order of several nanometers [5]. For this dimension, both macroscopic and hydrodynamic descriptions are possible.

At time $t = 0$, let the cavity radius begin to change by the law $R = R(t)$. It is necessary to find the distribution of the component S around the spherical cavity for the subsequent times. Let us consider the laminar flow of an ideal incompressible solution around the spherical cavity. The effect of adsorption on the motion of the cavity boundary due to variation of the surface-tension coefficient is neglected. Since the solution is dilute, the weak heat effects of dissolution and adsorption are ignored. Thus, in the formulation of the problem, there are no heat sources, and the temperature field is uniform. Together with the condition of the solution incompressibility, this means that the nonequilibrium cross effects are absent (thermo- and barodiffusion).

Governing Equations and Their Relationships. In this formulation, the admixture distribution around the spherical cavity is described by the diffusion equation in the potential field of the adsorption layer taking into account convective transfer of the admixture by the radial flow of the solution. We use the well-known adsorption-layer approximation [5, 6], which agrees well with the experimental data. For this, we distinguish the adsorption layer $R \leq r \leq R + \Delta$ of thickness $\Delta \ll R$ in which the state of the admixture is determined by the average concentration in the layer:

$$\langle c \rangle = \Delta^{-1} R^{-2} \int_R^{R+\Delta} c_S(r) r^2 dr.$$

A closed kinetic equation for $\langle c \rangle$ is derived from the initial equation of diffusion in the potential field of the adsorption layer if we adopt the hypothesis on “fast mixing” of particles in the layer [smallness of derivatives of $c_S(r)$ higher than the first order]. As a result, we obtain the Langmuir equation [5, 6] in which the kinetic parameters α (frequency of particle transition from the external boundary into the layer) and β (frequency of particle transition from the layer to the external boundary) are expressed in terms of layer thickness, the diffusion coefficient for admixture molecules D , and the parameters of the potential fields of the adsorption layer. Since the parameters of the potential field of the adsorption layer are insufficiently precise, we assume that α and β are phenomenological parameters.

Using the Langmuir exchange model, it is easy to obtain an equation for $\langle c \rangle$ from the balance relations for the number of particles entering and leaving the adsorption layer. In these cases, the equations for cavity expansion and compression have different forms because of the different effects of the flow of the solution on the admixture average concentration in the adsorption layer. For cavity expansion, we have the equation (ignoring the saturation of the adsorption layer)

$$\frac{d\langle c \rangle}{dt} = -\left(\beta + 2R^{-1} \frac{dR}{dt}\right) \langle c \rangle + \left(\alpha + 2R^{-1} \frac{dR}{dt}\right) c_\Delta, \quad (1)$$

where c_Δ is the admixture concentration at the external boundary of the layer. For cavity compression, we have the ordinary Langmuir equation

$$\frac{d\langle c \rangle}{dt} = -\beta \langle c \rangle + \alpha c_\Delta. \quad (2)$$

In the range of $r \geq R + \Delta$, the potential field of the adsorption layer does not act, and the equation for the admixture concentration c (the subscript S is omitted) becomes

$$\frac{\partial c}{\partial t} + \frac{dR}{dt} \frac{R^2}{r^2} \frac{\partial c}{\partial r} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right). \quad (3)$$

The boundary condition for Eq. (3) at the external boundary of the adsorption layer results from the condition of preservation of the total number of particles in the volume. Using Eqs. (1)–(3) and taking into account a rapid decrease in molecular flux with increase in r , we obtain the following equations:

— for cavity expansion,

$$D\Delta^{-1} \frac{\partial c}{\partial r} \Big|_{r=R+\Delta} = -\beta \langle c \rangle + \alpha c_\Delta;$$

— for cavity compression,

$$D\Delta^{-1} \frac{\partial c}{\partial r} \Big|_{r=R+\Delta} = -\left(\beta - 2R^{-1} \frac{dR}{dt}\right) \langle c \rangle + \left(\alpha - 2R^{-1} \frac{dR}{dt}\right) c_\Delta.$$

The initial conditions for Eqs. (1)–(3) have the form

$$\langle c \rangle|_{t=0} = Ac_0, \quad c(0, r) = c_0, \quad A = \alpha\beta^{-1},$$

where A is the adsorption coefficient.

We convert to the desired dimensionless quantities $x = \langle c \rangle / (Ac_0)$ and $y = c/c_0$ and the dimensionless variables $t_1 = \beta t$, $\eta = r/R$, and $a = R/R_0$. We introduce the Fourier numbers $\text{Fo}_1 = D/(\beta\Delta^2)$ and $\text{Fo}_2 = D/(\beta R_0^2)$ and the adsorption Peclet number $\text{Pe}_a(t_1) = 2a^{-1} da/dt_1$, which is the product of the diffusion Peclet number Pe_d and Fo_2 . For cavity expansion ($\text{Pe}_a > 0$), we obtain the following system of equations for the relative admixture concentration:

$$\begin{aligned} \frac{dx}{dt_1} &= -(1 + \text{Pe}_a)x + (1 + A^{-1}\text{Pe}_a)y_\Delta, \\ a^2 \left[\frac{\partial y}{\partial t_1} - \frac{1}{2} \text{Pe}_a \left(\eta - \frac{1}{\eta^2} \right) \frac{\partial y}{\partial \eta} \right] &= \text{Fo}_2 \left(\frac{\partial^2 y}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial y}{\partial \eta} \right), \\ \sqrt{\text{Fo}_1 \text{Fo}_2} \frac{\partial y}{\partial \eta} \Big|_{\eta=1+\sqrt{\text{Fo}_2}/(\sqrt{\text{Fo}_1 a})} &= Aa(y_\Delta - x), \quad x(0) = 1, \quad y(0, \eta) = 1. \end{aligned} \quad (4)$$

For cavity compression ($\text{Pe}_a < 0$), the kinetic equation for x and the boundary condition for y change as follows:

$$\begin{aligned} \frac{dx}{dt_1} &= y_\Delta - x, \\ \sqrt{\text{Fo}_1 \text{Fo}_2} \frac{\partial y}{\partial \eta} \Big|_{\eta=1+\sqrt{\text{Fo}_2}/(\sqrt{\text{Fo}_1 a})} &= Aa[-(1 - \text{Pe}_a)x + (1 - A^{-1}\text{Pe}_a)y_\Delta]. \end{aligned}$$

Let us estimate the parameters of the problem included in system (4). For most substances, the value of the adsorption coefficient ($A > 1$ for positive adsorption and $A < 1$ for negative adsorption) lies in the range of $A \approx 0.5$ –2. Hence, the values of the coefficients in Eqs. (4) expressed in terms of the above coefficient are of the order of unity. The Fourier number Fo_1 , which corresponds to the ratio of the characteristic time of departure of an admixture molecule from the adsorption layer to the characteristic time of diffusion in this layer, is also of the order of unity. The Fourier number Fo_2 , which corresponds to the ratio of the characteristic time of establishing adsorption equilibrium to the characteristic time of establishing a steady diffusion flow around the cavity, is of the order of Δ^2/R_0^2 and, hence, $\text{Fo}_2 \ll 1$.

Boundary-Layer Approximation. Using the smallness of the parameter Fo_2 at the highest derivative in the diffusion equation, we introduce the variable $\xi = (\eta - 1)/\sqrt{\text{Fo}_2}$. A reason for this introduction is that in the intense fast processes studied, the major disturbance of adsorption equilibrium occurs in a thin diffusion layer.

We seek a solution of the problem for x and y in the form of the asymptotic series

$$x = x^{(0)} + \sqrt{\text{Fo}_2} x^{(1)} + \dots, \quad y = y^{(0)} + \sqrt{\text{Fo}_2} y^{(1)} + \dots$$

Then, for the zeroth approximation subject to the condition $\text{Pe}_a \gg \sqrt{\text{Fo}_2}$, we have the following equations:

— for cavity expansion,

$$\frac{dx^{(0)}}{dt_1} = -(1 + \text{Pe}_a)x^{(0)} + (1 + A^{-1}\text{Pe}_a)y_\Delta^{(0)}, \quad a^2 \left[\frac{\partial y^{(0)}}{\partial t_1} - \frac{3}{2} \text{Pe}_a \xi \frac{\partial y^{(0)}}{\partial \xi} \right] = \frac{\partial^2 y^{(0)}}{\partial \xi^2}, \quad (5)$$

$$\sqrt{\text{Fo}_1} \frac{\partial y^{(0)}}{\partial \xi} \Big|_{\xi=1/(\sqrt{\text{Fo}_1 a})} = Aa(y_\Delta^{(0)} - x^{(0)}), \quad x^{(0)}(0) = 1, \quad y^{(0)}(0, \xi) = 1;$$

— for cavity compression (subject to the additional condition $a \gg \sqrt{\text{Fo}_2}$),

$$\frac{dx^{(0)}}{dt_1} = y_\Delta^{(0)} - x^{(0)}, \quad (6)$$

$$\sqrt{\text{Fo}_1} \frac{\partial y^{(0)}}{\partial \xi} \Big|_{\xi=1/(\sqrt{\text{Fo}_1 a})} = Aa[-(1 - \text{Pe}_a)x^{(0)} + (1 - A^{-1}\text{Pe}_a)y_\Delta^{(0)}].$$

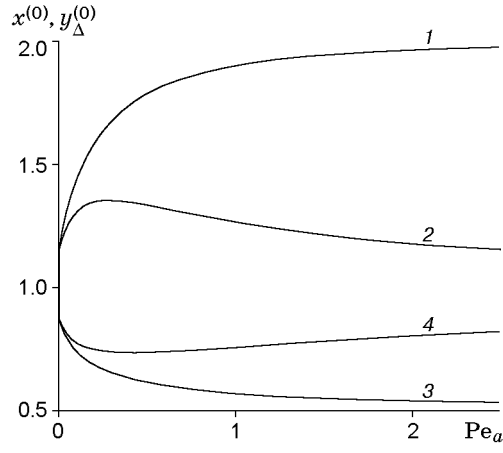


Fig. 1. Curves of $x^{(0)}(\text{Pe}_a)$ (1 and 3) and $y_{\Delta}^{(0)}(\text{Pe}_a)$ (2 and 4) for the self-similar solution for negative adsorption (curves 1 and 2) for $A = 0.5$ and $\text{Fo}_1 = 0.25$ and positive adsorption (curves 3 and 4) for $A = 2$ and $\text{Fo}_1 = 1$.

Converting in Eqs. (5) and (6) to the Plesset–Zwick variables known for the problem of the dynamics of vapor bubble growth [7], we have

$$\tau = \int_0^{t_1} a^4(s) ds, \quad z = a^3 \xi;$$

for cavity expansion, we obtain

$$\frac{dx^{(0)}}{d\tau} = -(a^{-4} + \text{Pe}_a)x^{(0)} + (a^{-4} + A^{-1}\text{Pe}_a)y_{\Delta}^{(0)}; \quad (7)$$

$$\frac{\partial y^{(0)}}{\partial \tau} = \frac{\partial^2 y^{(0)}}{\partial z^2}, \quad (8)$$

$$a^2 \sqrt{\text{Fo}_1} \frac{\partial y^{(0)}}{\partial z} \Big|_{z=a^2/\sqrt{\text{Fo}_1}} = A(y_{\Delta}^{(0)} - x^{(0)}), \quad x^{(0)}(0) = 1, \quad y^{(0)}(0, z) = 1, \quad (9)$$

and for compression,

$$\frac{dx^{(0)}}{d\tau} = a^{-4}(y_{\Delta}^{(0)} - x^{(0)}), \quad (10)$$

$$a^2 \sqrt{\text{Fo}_1} \frac{\partial y^{(0)}}{\partial z} \Big|_{z=a^2/\sqrt{\text{Fo}_1}} = A[-(1 - a^4 \text{Pe}_a)x^{(0)} + (1 - A^{-1}a^4 \text{Pe}_a)y_{\Delta}^{(0)}].$$

Self-Similar Solution. For exponential expansion of the cavity (for example, at the leading edge of the shock wave), under the law $a(t_1) = \exp(\text{Pe}_a t_1/2)$ [hence, $a(\tau) = (1 + 2\text{Pe}_a \tau)^{1/4}$, where $\text{Pe}_a > 0$ is constant], the problem has a self-similar solution in the form $y^{(0)}(z, \tau) = \varphi(z/a^2)$, $y_{\Delta}^{(0)}$, $x^{(0)} = \text{const}(\tau)$ for $t_1 > \text{Pe}_a^{-1}$. Representing the solution in the above form, from Eqs. (7) and (8) and boundary condition (9), we find

$$x^{(0)} = \frac{2A^{-1}\sqrt{\text{Fo}_1}(A + \text{Pe}_a)}{\sqrt{2\pi\text{Pe}_a}(A - 1) \text{erfc}(\sqrt{\text{Pe}_a/(2\text{Fo}_1)}) \exp(\text{Pe}_a/(2\text{Fo}_1)) + 2\sqrt{\text{Fo}_1}(1 + \text{Pe}_a)},$$

$$y_{\Delta}^{(0)} = \frac{2\sqrt{\text{Fo}_1}(1 + \text{Pe}_a)}{\sqrt{2\pi\text{Pe}_a}(A - 1) \text{erfc}(\sqrt{\text{Pe}_a/(2\text{Fo}_1)}) \exp(\text{Pe}_a/(2\text{Fo}_1)) + 2\sqrt{\text{Fo}_1}(1 + \text{Pe}_a)},$$

where $\text{erfc}(w)$ is the additional probability integral.

Figure 1 shows curves of $x^{(0)}(\text{Pe}_a)$ and $y_{\Delta}^{(0)}(\text{Pe}_a)$. Of interest is the behavior of the quantity $y_{\Delta}^{(0)}$ because in the case of cavity expansion, the average admixture concentration in the adsorption layer cannot be either higher (for $A < 1$) or lower (for $A > 1$) than the equilibrium concentration in the bulk; the quantity $x^{(0)}$ is limited by

the value of A^{-1} . As follows from the analytical dependence and the data in Fig. 1, for negative adsorption, $y_{\Delta}^{(0)}$ first increases as $1 + (1 - A)\sqrt{\pi\text{Pe}_a/(2\text{Fo}_1)}$ with increase in Pe_a , and, for $\text{Pe}_a > 0.25$, it gradually decreases to its equilibrium value $y_{\Delta}^{(0)} = 1$. For positive adsorption, $y_{\Delta}^{(0)}$ first decreases as $1 - (A - 1)\sqrt{\pi\text{Pe}_a/(2\text{Fo}_1)}$ with increase in Pe_a , and for $\text{Pe}_a > 0.25$, it gradually increases to its equilibrium value $y_{\Delta}^{(0)} = 1$. Such behavior of the solution for $\text{Pe}_a > 0.25$ is due to the fact that the disturbance of the equilibrium in the adsorption layer is “saturated,” and the flow has enough time to remove the admixture molecules from the thin diffusion layer to the adsorption layer. Hence, the quantity $y_{\Delta}^{(0)}$ tends to the equilibrium value $y_{\Delta}^{(0)} = 1$. Thus, during cavity expansion, the variation of solution saturation in the external diffusion layer is limited and reaches a maximum at a certain Peclet number $\text{Pe}_a^*(\text{Fo}_1, A)$. This is due to the various effects of the flow on the admixture in the adsorption and external diffusion layers and to the existence of a maximum possible disturbance of the equilibrium in the adsorption layer.

Numerical Solution. For an arbitrary curve $a(t_1)$, the solution of the diffusion equation (8) with boundary and initial condition (9) can be written in terms of the simple-layer potential:

$$y^{(0)}(\tau, z) = 1 + \frac{1}{4\sqrt{\pi}} \int_0^{\tau} \frac{\nu(\lambda)}{\sqrt{\tau - \lambda}} \exp\left(-\frac{(z - a^2(\lambda))^2}{4(\tau - \lambda)}\right) d\lambda.$$

Then, following a standard procedure [8], we obtain the following integral equation for the function $\nu(\tau)$:

$$\nu(\tau) = \frac{4A(x^{(0)} - 1)}{a^2\sqrt{\text{Fo}_1}} - \int_0^{\tau} (a^2(\tau) - a^2(\lambda))\nu(\lambda)G(\tau, \lambda) d\lambda - \frac{2A}{a^2} \int_0^{\tau} (\tau - \lambda)\nu(\lambda)G(\tau, \lambda) d\lambda, \quad (11)$$

$$G(\tau, \lambda) = \frac{1}{2\sqrt{\pi\text{Fo}_1}(\tau - \lambda)^3} \exp\left(-\frac{(a^2(\tau) - a^2(\lambda))^2}{4\text{Fo}_1(\tau - \lambda)}\right),$$

which determines the solution of the problem together with the kinetic equation (7). A similar integral equation can be written for cavity compression (in this paper, this equation is omitted).

Equations (7), (10), and (11) were solved numerically for various dependences $a(t_1)$. Equations (7) and (10) were solved by the fourth-order Runge–Kutta method, and the integral equation (11) was solved by successive cyclic integration using the open-type Newton–Cotes formula for numerical integration. The numerical scheme was tested on the self-similar solution for exponential cavity expansion in the solution and showed good agreement of numerical and analytical solutions with an error typical of errors for the Runge–Kutta method and the open-type Newton–Cotes formulas.

The case of expansion was studied for the time dependence of the cavity radius in the form $a(t_1) = (1 + vt_1)^\gamma$; hence, $a(\tau) = [1 + (4\gamma + 1)v\tau]^{\gamma/(4\gamma + 1)}$. The time dependence of the Peclet number has the form $\text{Pe}_a = 2v\gamma \times (1 + vt_1)^{-1}$. It is established that for negative adsorption, $y_{\Delta}^{(0)}$ increases to a maximum value $y_{\Delta\text{max}}^{(0)}$, and, then, decreases to the equilibrium value $y_{\Delta}^{(0)} = 1$. Positive adsorption is characterized by a minimum value $y_{\Delta\text{min}}^{(0)}$. In the range of $\text{Pe}_a(0) < 1$, we have $y_{\Delta\text{max}}^{(0)} \sim 1 + (1 - A)\sqrt{\text{Pe}_a(0)/\text{Fo}_1} = 1 + (1 - A)\sqrt{2v\gamma/\text{Fo}_1}$ and $y_{\Delta\text{min}}^{(0)} \sim 1 - (A - 1)\sqrt{\text{Pe}_a(0)/\text{Fo}_1} = 1 - (A - 1)\sqrt{2v\gamma/\text{Fo}_1}$. The behavior of the quantity $y_{\Delta}^{(0)}$ corresponds to the time variation of the Peclet number $\text{Pe}_a(t_1)$, which decreases asymptotically as t_1^{-1} , leading obviously to the recovery of adsorption equilibrium. Figure 2 gives results of numerical calculation in the case of linear increase in cavity radius ($\gamma = 1$).

The case of compression was considered for variation of the cavity radius by the Rayleigh law $\text{Pe}_a(t_1) = -1.83(a\beta T)^{-1}\sqrt{2(a^{-3} - 1)/3}$ (T is the time of filling the cavity) [9]. Figure 3 gives calculation results. It is obvious that in the case of cavity compression, the behavior of the quantities $x^{(0)}$ and $y_{\Delta}^{(0)}$ is opposite to that in the case of expansion: slow variation in the initial stage and then rapid growth (for positive adsorption) or abrupt decrease (for negative adsorption). Since for cavity compression under the Rayleigh law, the absolute value of the Peclet number $|\text{Pe}_a(t_1)|$ increases constantly (from zero at the initial time to infinity during cavity collapse), we analyze the behavior of the quantities $x^{(0)}$ and $y_{\Delta}^{(0)}$ which variation in Pe_a .

If the diffusion flow component at the external boundary of the adsorption layer is assumed to be of the order of unity, the convective component is of the order of the Peclet number Pe_a . For $|\text{Pe}_a| \ll 1$, the convective component is small and the diffusion flow of admixture molecules from the external boundary of the adsorption layer sustains the quasiequilibrium state. With increase in Peclet number to $|\text{Pe}_a| \sim 1$, the convective and diffusion flux components at the external boundary take values of the same order: the diffusion flow of admixture molecules

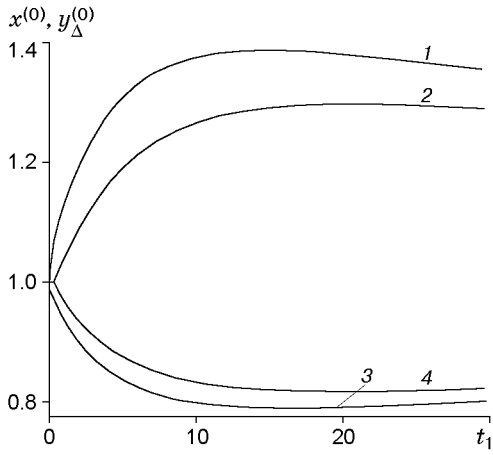


Fig. 2

Fig. 2. Curves of $x^{(0)}(t_1)$ and $y_{\Delta}^{(0)}(t_1)$ for linear cavity expansion ($\gamma = 1$ and $v = 0.1$) (notation the same as in Fig. 1).

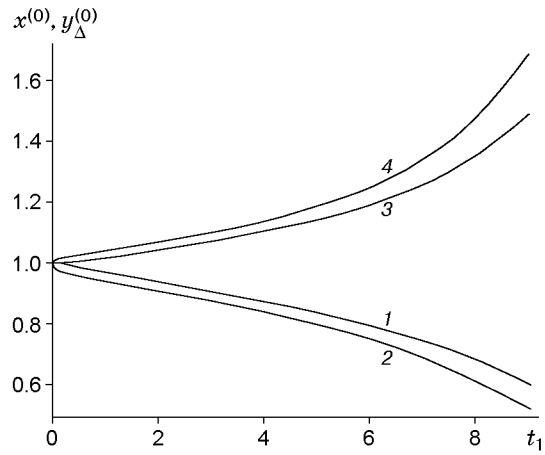


Fig. 3

Fig. 3. Curves of $x^{(0)}(t_1)$ and $y_{\Delta}^{(0)}(t_1)$ for cavity compression under the Rayleigh law ($\beta T = 15$) (notation the same as in Fig. 1).

from the external boundary is compensated for by the convective flow of these molecules from the adsorption layer. In this range of Peclet numbers, a quasisteady slowly increasing or decreasing solution for $x^{(0)}$ and $y_{\Delta}^{(0)}$ is established. Equating the diffusion and convective flow components in the vicinity of the external boundary of the adsorption layer and taking the boundary condition into account, we find that $x^{(0)} \sim y_{\Delta}^{(0)} \sim A$. For large absolute values of the Peclet number ($|\text{Pe}_a| \gg 1$), in the case of compression, we can neglect the diffusion flow component in Eq. (5) $\partial^2 y^{(0)} / \partial \xi^2$ and convert to a system of kinetic equations for $x^{(0)}$ and $y_{\Delta}^{(0)}$.

We consider the equations for an exponential law of decrease in cavity radius $a(t_1) = \exp(\text{Pe}_a t_1 / 2)$, which holds when a shock wave approaches the cavity. By virtue of the constancy of $\text{Pe}_a < 0$, the analysis is simplified, and the results obtained are valid for any $|\text{Pe}_a(t_1)| \gg 1$. From Eqs. (5) and (6) and the corresponding boundary condition, we have

$$\frac{dx^{(0)}}{dt_1} = y_{\Delta}^{(0)} - x^{(0)}, \quad \frac{dy_{\Delta}^{(0)}}{dt_1} = \frac{3\text{Pe}_a^2}{2\text{Fo}_1} (Ax^{(0)} - y_{\Delta}^{(0)}). \quad (12)$$

The characteristic indices of Eqs. (12) have the form

$$\mu_{\pm} = -(G + 1)/2 \pm ((G + 1)^2/4 + G(A - 1))^{1/2} \quad [G = 3\text{Pe}_a^2/(2\text{Fo}_1)].$$

The positive characteristic index is $\mu_+ \approx A - 1$ (with accuracy up to G^{-1}). Hence, for large absolute values of the Peclet number ($|\text{Pe}_a| \gg 1$), the adsorption kinetics is determined only by the adsorption coefficient, and the relative admixture concentration both in the adsorption layer and on its external boundary increases ($A > 1$) or decreases ($A < 1$) exponentially: $x^{(0)}, y_{\Delta}^{(0)} \sim \exp((A - 1)t_1) = \exp((\alpha - \beta)t)$. We note that for $|\text{Pe}_a| \gg 1$, the effect of the solution flow on admixture distribution in the adsorption layer should be taken into account, and, hence, the exact problem of admixture diffusion in the potential field of the adsorption layer must be solved.

An essential difference in the adsorption kinetics during cavity expansion and compression leads to the problem of dynamic adsorption in the case of alternating compression and expansion, in particular, cavity pulsations (for example, after passage of a shock wave or in an ultrasonic field). Figure 4 gives calculation results for the problem in which weakly nonlinear pulsations are simulated by time variation of cavity radius τ in the form $a(\tau) = 1 + f \sin v\tau$ ($f < 1$) and $\text{Pe}_a \sim 2fv \cos v\tau$ [a corresponding curve of $a(t_1)$ is shown in Fig. 4a]. For positive adsorption (Fig. 4b), the relative admixture concentration averaged over the period grows both in the adsorption layer $\langle x^{(0)} \rangle_T$ and on its external boundary $\langle y_{\Delta}^{(0)} \rangle_T$ ("pumping" of the admixture). For negative adsorption, an opposite dependence is observed (Fig. 4c). In Fig. 4b and c, the curves of $x^{(0)}(t_1)$ and $y_{\Delta}^{(0)}(t_1)$ virtually coincide. With time, the relative admixture concentration averaged over the period decreases or increases more slowly and then attains saturation.

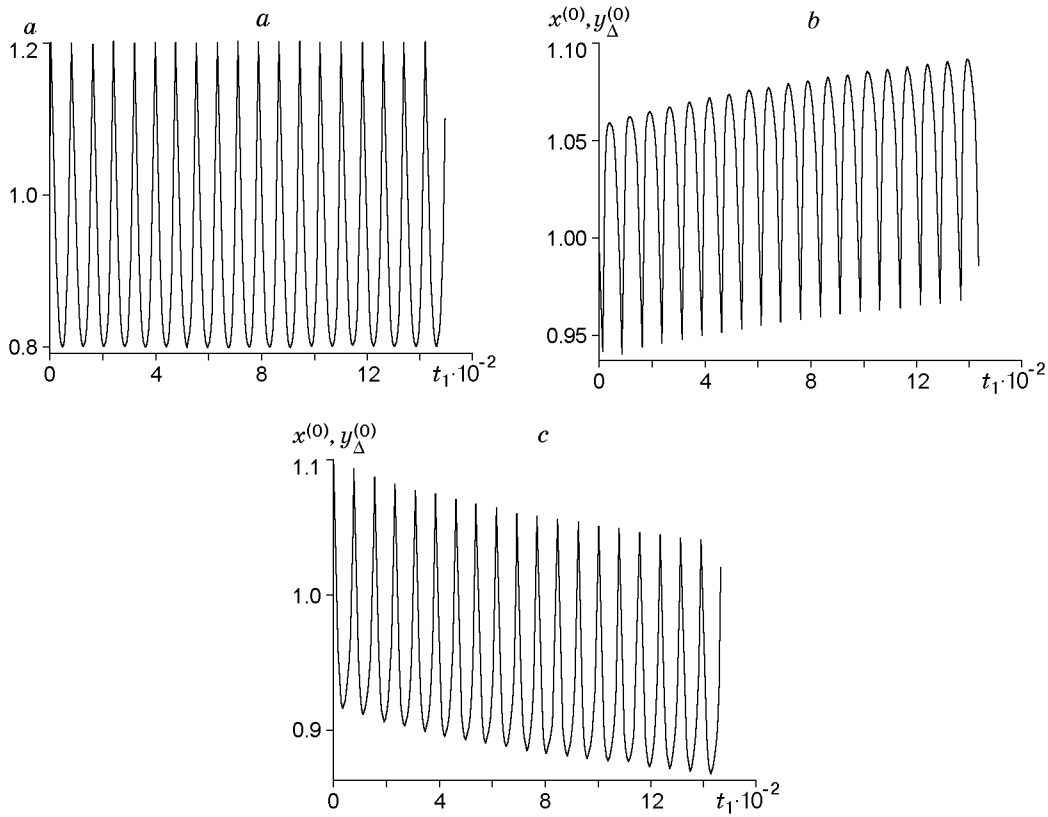


Fig. 4. Results of numerical solution of the problem of dynamic adsorption with the law $a(\tau) = 1 + f \sin v\tau$ simulating weak nonlinear pulsations for $v = 0.1$ and $f = 0.2$: (a) $a(t_1)$; (b) $x^{(0)}(t_1)$ and $y_{\Delta}^{(0)}(t_1)$ for positive adsorption ($A = 2$ and $Fo_1 = 1$); (c) $x^{(0)}(t_1)$ and $y_{\Delta}^{(0)}(t_1)$ for negative adsorption ($A = 0.5$ and $Fo_1 = 0.25$).

An increase in the amplitude of the Peclet number Pe_a leads to higher velocities of “pumping” and larger values of $\langle x^{(0)} \rangle_T$ and $\langle y_{\Delta}^{(0)} \rangle_T$ in the saturation limit.

The solution of the problem obtained for cavity pulsations describes the process of “straightened” adsorption by analogy to the well-known processes of “straightened” heat transfer for oscillating vapor bubbles and “straightened” diffusion for vapor bubbles oscillating in a liquid [10].

Discussion of Results. Local variation of the saturation of a dilute solution is established for radial flow of a liquid around a spherical cavity. For cavity expansion, the variation of saturation is limited and reaches a maximum at a certain Peclet number Pe_a^* . For cavity compression, the variation of saturation is limited only by the time of filling the cavity and can reach large values at $|Pe_a| \gg 1$. For cavity pulsations, a limited increase (for positive adsorption) or decrease (for negative adsorption) in the admixture concentration averaged over the period is observed in the adsorption layer and on its external boundary (the process of “straightened” adsorption).

The velocity of the cavity wall u necessary for substantial disturbance of adsorption equilibrium is estimated from the condition $Pe_a \gg \sqrt{Fo_2}$, which satisfies the condition $u \gg u_* = \sqrt{\beta D}$. For characteristic values of the parameters $\beta \approx 10^7 \text{ sec}^{-1}$ and $D \approx 10^{-9} \text{ m}^2/\text{sec}$, we have $u_* = 0.1 \text{ m/sec}$. The cavity-wall velocity upon passage of the shock wave is $u \sim \sqrt{p_0/\rho}$ (p_0 is the pressure amplitude in the liquid and ρ is the liquid density), and $u = 10\text{--}100 \text{ m/sec}$ for $p_0 = 0.1\text{--}10 \text{ MPa}$, respectively ($\rho = 10^3 \text{ kg/m}^3$). For a cavity of radius $R \approx 10 \text{ }\mu\text{m}$, these cavity-wall velocities correspond to the adsorption Peclet number $Pe_a \sim 1$. For a cavity of radius R_0 , pulsating with frequency ω and amplitude δR , the necessary condition has the form $\delta R \omega \sim \sqrt{p_0/\rho} \delta R/R_0 \gg u_*$, where p_0 corresponds, for example, to the pressure amplitude in an acoustic field. Hence, the relative pulsation amplitude $\delta R/R_0$ should not be too small. This is the case for resonance excitation of small gas bubbles ($R_0 \approx 10\text{--}100 \text{ }\mu\text{m}$) oscillating at a frequency $\omega \approx 10^5\text{--}10^6 \text{ Hz}$, which corresponds to ultrasonic frequency. Thus, the physical conditions necessary for the occurrence of the processes considered are achieved by passage of a shock

wave through a solution containing small gas bubbles or by the action of an intense ultrasonic field, in particular, excitation in of cavitation in the solution.

The local variation of saturation for radial flow of a solution around a cavity established in the present paper can significantly affect the kinetics of some physicochemical processes in gas-liquid media. Upon expansion or compression of cavities, these can be fast chemical reactions ($t \approx 10^{-6}$ – 10^{-5} sec) with the participation of radicals. For cavity pulsations (at the end of a sufficiently strong shock wave or in an intense ultrasonic field), the variation of solution saturation can affect physicochemical processes occurring for characteristic times $t \approx 10^{-3}$ – 10^{-1} sec. In particular, a local increase in the oversaturation of the solution around a cavity leads to a significant decrease in the induction period of solid-phase extraction due to rapid (exponential) growth in nucleation frequency with increase in the degree of oversaturation.

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