

Mass transfer across the free surface of a wavy film limited by mass exchange in the liquid is investigated in the thin diffusional layer approximation.

Heat- and mass-transfer processes with the participation of thin liquid layers are used in various instruments of chemical technology, in energetics, cryogenics, metallurgy, and other branches. The flow rate of these processes is determined, to a large extent, by the flow regime in the film, and, in particular, for laminar films it depends substantially on the characteristics of the waves generated in them. This dependence is particularly strong if most of the transport resistance is concentrated near the free surface of the film, as is the case in the very common processes of physical absorption and desorption of gases by liquid films (see, for example, [1-10]).

Since the molecular diffusion coefficients of dissolved gases are small, the kinetics of sorption or desorption is limited by the diffusion rate in a thin layer, adjacent to the free surface of the film, and corresponding to a Peclet number much larger than unity in real situations. The latter justifies the use of the well-known thin diffusional layer approximation [11-15] in the theoretical analysis of these processes. However, the corresponding problem of convective diffusion was earlier solved either too crudely, with loss of or excess accuracy [11, 12], or additional, quite restrictive assumptions were used in them on wave harmonicity [13, 14], in-phase oscillations of the width of the diffusional layer by wave pulsations of the film width [13], a continuous growth of the diffusional layer independently of the wave phase [15], etc.

The known theoretical dependences of this type lead to substantial lowering (in comparison with experiment) of the parameter values characterizing the intensity of mass exchange. Therefore the literature contains models [15-17] in which one assumes eddy formation and practically total mixing in saddle-shaped waves: the growth from a saddle point of a diffusional boundary layer is destroyed till one reaches the following saddle point, where it is lowered by the new such layer. The conclusion on eddy formation could follow from the concept that a change in sign of the longitudinal component of the liquid velocity is possible near the saddle point [1]. However, these concepts were verified neither by more accurate theoretical analysis (see, for example, [18]), nor by direct measurements of the velocity profile in the film [19-21], and were therefore recently criticized in [10]. It follows from the theory suggested below that to derive theoretical dependences in agreement with experimental data it is not necessary to make any assumptions concerning eddy mixing in laminar films with moderate Reynolds number values.

To describe the stationary wave flow regime in the film we use the theory of weakly nonlinear waves [22], according to which the film width h and the longitudinal velocity component v_ξ at the free surface $\eta = h$ are assumed in the form

$$h = h_0(1 + \varphi), \quad v_\xi|_{\eta=h} = u_0 F, \quad F = (3/2)(1 + \psi), \quad (1)$$

$$\varphi = \sum_{m=-2}^2 \Phi_m \exp \left[i \frac{mk}{\lambda} (cu_0 \tau - \xi) \right], \quad \psi = \sum_{m=-2}^2 \Psi_m \exp \left[i \frac{mk}{\lambda} (cu_0 \tau - \xi) \right],$$

where u_0 and h_0 are the mean velocity and width of the laminar nonwavy film, and c and k are the dimensionless wave velocity and wave number (the size of the wavelength being $\lambda = (2\pi/k)h_0$).

Two variants of the theory were considered in [22]: a rigorous flow study by the small parameter method, valid for $\varepsilon Re \ll \varphi \ll 1$ ($\varepsilon = h_0/\lambda$, $Re = u_0 h_0/\nu$), and an approximate study, in which

TABLE 1. Stationary Wave Parameters for Small Reynolds Numbers (the small parameter method): I-IV, Water and Aqueous Glycerine Solutions, $Fi^{0.1} = 11.34, 10.94, 7.74, \text{ and } 3.98$; the Digits in the Columns of the Table are the Values of $k, c, 10^2q, \text{ and } \ast$, Respectively

Re	$\alpha=0$				$\alpha=\pi/4$			
	I	II	III	IV	I	II	III	IV
1	0,0243	0,0259	0,0478	0,1378	0,0086	0,0091	0,0171	0,0487
	2,9984	2,9981	2,9925	2,9364	3,0000	3,0000	2,9996	2,9959
	0,0038	0,0043	0,0135	0,1093	0,0000	0,0000	0,0001	0,0007
	1,0002	1,0003	1,0008	1,0071	1,0000	1,0000	1,0000	1,0000
3	0,0641	0,0682	0,1216	0,2198	0,0509	0,0543	0,0980	0,2273
	2,9382	2,9304	2,7998	2,4517	2,9745	2,9710	2,9093	2,5961
	0,1996	0,2232	0,5982	1,3584	0,0688	0,0772	0,2208	0,7148
	1,0130	1,0147	1,0475	1,1993	1,0043	1,0048	1,0150	1,0787
5	0,0982	0,1040	0,1687	—	0,0856	0,0908	0,1542	—
	2,6700	2,6686	2,3314	—	2,8116	2,7916	2,5264	—
	1,0020	1,0827	1,6256	—	0,5785	0,6337	1,1569	—
	1,0931	1,1053	1,2966	—	1,0452	1,0510	1,1434	—

the distribution of the longitudinal velocity component over the film width was approximated by a self-similar parabolic profile, providing fair results even for $\varepsilon Re \gg 1$. In both cases it was assumed that $\varepsilon \ll 1$, i.e., long waves were considered.

In the small parameter method we have for the series coefficients (1), characterizing the established wave regime ($\varepsilon Re \ll 1$):

$$\begin{aligned}
 \Phi_0 &= -2q, \Phi_1 = \sqrt{q}, \Phi_2 = \frac{3}{2} \left[2i - \frac{We k^3}{\cos \alpha} - \left(\operatorname{tg} \alpha - \frac{23}{20} \operatorname{Re} \right) k \right] \times \\
 &\times \left\{ i \left[c - 3 - \frac{90}{7} \frac{We \operatorname{Re}}{\cos \alpha} k^4 + 12k^2 \left(1 + \frac{9}{28} \operatorname{Re}^2 - \frac{15}{56} \operatorname{Re} \operatorname{tg} \alpha \right) \right] - \right. \\
 &\quad \left. - \frac{5}{4} \operatorname{Re} c k + 2 \left(\operatorname{tg} \alpha + \frac{27}{40} \operatorname{Re} \right) k + \frac{8 We k^3}{\cos \alpha} \right\}^{-1} q, \Psi_0 = 2q, \\
 \Psi_1 &= \left\{ 2 + ik \left[\frac{We k^2}{\cos \alpha} + \operatorname{tg} \alpha - \frac{2}{3} \operatorname{Re} \left(c - \frac{9}{8} \right) \right] \right\} \sqrt{q}, \\
 \Psi_2 &= q + 2\Phi_2 \left\{ 1 + ik \left[\frac{4 We k^2}{\cos \alpha} + \operatorname{tg} \alpha - \frac{2}{3} \operatorname{Re} \left(c - \frac{9}{8} \right) \right] \right\}.
 \end{aligned} \tag{2}$$

Within the integral relation method ($\varepsilon Re \gg 1$):

$$\begin{aligned}
 \Phi_0 &= 2 \left(1 - \frac{2}{3} c \right) q, \Phi_1 = \sqrt{q}, \Phi_2 = \left[2E_2(c-1)^2 + 6(c-1) - 3 + 3ik \operatorname{tg} \alpha + \frac{3i We}{\cos \alpha} k^3 \right] G^{-1} q, \Psi_0 = -\frac{2}{3} cq, \\
 \Psi_1 &= (c-1) \sqrt{q}, \Psi_2 = [2E_2(c-1)^2 + (2E-3)(c-1) + \\
 &\quad + 3 + 9ik \operatorname{tg} \alpha - 2E_1 + \frac{27i We}{\cos \alpha} k^3] (c-1) G^{-1} q, \\
 G &= (2E+3)(c-1) - 6(1+ik \operatorname{tg} \alpha) + 2E_1 - \frac{24i We}{\cos \alpha} k^3, \\
 E &= i \operatorname{Re} \left(c - \frac{12}{5} \right) k, E_1 = i \operatorname{Re} \left(c - \frac{6}{5} \right) k, E_2 = \frac{6}{5} i \operatorname{Re} k.
 \end{aligned} \tag{3}$$

Here the Reynolds and film numbers were introduced

$$\operatorname{Re} = \frac{u_0 h_0}{\nu}, \operatorname{Fi} = \frac{\sigma^3}{\rho^3 \nu^4 g} = 9 \operatorname{Re}^2 \operatorname{We}^3 / \cos^2 \alpha. \tag{4}$$

In both cases the indicated coefficients are single-valued functions of k and c , as well as of the square q of the main harmonic amplitude of the dimensionless perturbation φ of the

TABLE 2. Stationary Wave Parameters for Moderate Reynolds Numbers (the integral relation method): I-IV, Water, Aqueous Solutions of Glycerine and Oil, $Fi^{0.1} = 11.34, 7.74, 3.98, \text{ and } 1.79$; the Digits in the Columns of the Table are the Values of $k, c, 10^2q, \text{ and } \kappa$, Respectively

Re	$\alpha=0$				$\alpha=\pi/4$			
	I	II	III	IV	I	II	III	IV
4	0,0662	0,1201	0,3115	0,9811	0,0548	0,0994	0,2709	0,8844
	2,9202	2,8004	2,4598	1,9787	2,9618	2,8922	2,6493	2,3179
	0,2936	0,7646	2,3871	5,3590	0,1197	0,3449	1,2228	2,6748
	1,0206	1,0544	1,1842	1,6295	1,0084	1,0243	1,0893	1,2208
8	0,1046	0,1822	0,4611	1,4446	0,0949	0,1668	0,4284	1,4071
	2,6164	2,3928	2,0025	1,6520	2,7007	2,5054	2,1693	1,9086
	1,5839	2,7606	5,2061	6,8486	1,1132	1,9870	3,7580	5,2120
	1,1165	1,2191	1,5878	4,0850	1,0805	1,1508	1,3461	1,7047
12	0,1326	0,2292	0,5778		0,1231	0,2141	0,5499	
	2,3539	2,1210	1,7805	—	2,4384	2,2246	1,9237	—
	2,9855	4,4319	6,5208		2,3789	3,5540	5,3171	
	1,2416	1,4281	2,3098		1,1851	1,3124	1,6950	
16	0,1561	0,2695	0,6778		0,1464	0,2541	0,6561	
	2,1604	1,9421	1,6646	—	2,2400	2,0361	1,7885	—
	4,1774	5,5940	6,8545		3,5167	4,7432	6,0791	
	1,3879	1,7038	3,7531		1,3055	1,5089	2,1822	
20	0,1771	0,3052	0,7655		0,1670	0,2898	0,7552	
	2,0170	1,8203	1,6033	—	2,0912	1,9058	1,7119	—
	5,1103	6,3195	6,6416		4,4506	5,5699	6,3204	
	1,5639	2,0935	6,4131		1,4446	1,7580	2,7959	

film width, which are, in turn uniquely determined by the Re and Fi values. These dependences are easily found on the basis of the results of [22]; data of numerical calculations of $k, c, \text{ and } q$ are given in Tables 1 and 2.

The equation of convective diffusion is in dimensional variables

$$\frac{\partial c}{\partial \tau} + v_{\xi} \frac{\partial c}{\partial \xi} + v_{\eta} \frac{\partial c}{\partial \eta} = D \left(\frac{\partial^2 c}{\partial \xi^2} + \frac{\partial^2 c}{\partial \eta^2} \right). \quad (5)$$

We introduce the dimensionless variables:

$$t = \frac{u_0}{\lambda} \tau, \quad x = \frac{\xi}{\lambda}, \quad y = \frac{h - \eta}{l}, \quad \left\{ \begin{matrix} v_x \\ v_y \end{matrix} \right\} = \frac{1}{u_0} \left\{ \begin{matrix} v_{\xi} \\ v_{\eta} \end{matrix} \right\}, \quad n = \frac{c}{c_*}. \quad (6)$$

In the variables (6) Eq. (5) is written as:

$$\begin{aligned} & \frac{\partial n}{\partial t} + v_y \frac{\partial n}{\partial x} + \left[-\frac{\lambda}{l} v_x + \frac{h_0}{l} \left(\frac{\partial \varphi}{\partial t} + v_x \frac{\partial \varphi}{\partial x} \right) \right] \frac{\partial n}{\partial y} = \\ & = \frac{\lambda^2}{l^2} \frac{D}{u_0 \lambda} \left\{ \left[1 + \frac{h_0^2}{\lambda^2} \left(\frac{\partial \varphi}{\partial x} \right)^2 \right] \frac{\partial^2 n}{\partial y^2} + \frac{l^2}{\lambda^2} \frac{\partial^2 n}{\partial x^2} + \frac{h_0 l}{\lambda^2} \left(2 \frac{\partial \varphi}{\partial x} \frac{\partial^2 n}{\partial x \partial y} + \frac{\partial^2 \varphi}{\partial x^2} \frac{\partial n}{\partial y} \right) \right\}. \end{aligned} \quad (7)$$

We assume that along with the inequality $\varepsilon = h_0/\lambda \ll 1$ the following inequality is valid, $l/h_0 \ll 1$. Based on the equations of continuity and kinematic conditions, valid on the free surface of the film, one has inside the thin diffusional boundary layer

$$v_{\eta} = \frac{\partial h}{\partial \tau} + v_{\xi} \left|_{\eta=h} \frac{\partial h}{\partial \xi} - \frac{\partial v_{\xi}}{\partial \xi} \right|_{\eta=h} (\eta - h)$$

or, in the variables (6) with account of the definition of φ in (1) we can write with the same accuracy

$$v_y = \frac{h_0}{\lambda} \left(\frac{\partial \varphi}{\partial t} + F \frac{\partial \varphi}{\partial x} \right) + \frac{l}{\lambda} \frac{\partial F}{\partial x} y. \quad (8)$$

The quantity l is defined as follows:

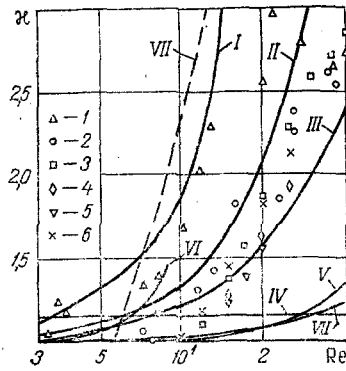


Fig. 1. The relative Sherwood number as a function of physical and regime parameters; 1-6) experiment: 1, 2) aqueous glycerine solutions, $Fi^{0.1} = 5.79; 7.74$ [10]; 3-6) water, $Fi^{0.1} = 11.34$, data of [24, 25, 26, and 27], respectively; I-III) Eq. (24) for aqueous glycerine solutions and water, $Fi^{0.1} = 3.98; 7.74; 11.34$; IV-VII) theory of [12, 13, 14, and 15], respectively, for water (the characteristic waves for V-VII are estimated from [22]); the dashed curve VII is the theory [15] for total mixing and restoration of diffusional layer.

$$l = \frac{\lambda}{\sqrt{Pe_\lambda}}, Pe_\lambda = \frac{3^3 u_0 \lambda}{2D}. \quad (9)$$

Using (8) and (9), and neglecting higher-order terms, we obtain from (7)

$$\frac{\partial n}{\partial t} + F \frac{\partial n}{\partial x} - y \frac{\partial F}{\partial x} \frac{\partial n}{\partial y} = \frac{3}{2} \frac{\partial^2 n}{\partial y^2}. \quad (10)$$

The boundary conditions imposed on the solutions of (10) are:

$$n = 0, y = 0; n = 1, x = 0; n \rightarrow 1, y \rightarrow \infty. \quad (11)$$

Initial conditions are not used in the problems considered; rather, one uses, as always in similar situations, the periodicity condition.

The validity conditions $\varepsilon \ll 1$ and $l/h_0 \ll 1$ of the problem stated of convective diffusion in the form (10), (11) are transformed to the form

$$\frac{k}{2\pi} \ll 1, Pe_\lambda \gg Re_\lambda^2 (Sc \gg Re_\lambda), Re_\lambda = \frac{u_0 \lambda}{\nu}. \quad (12)$$

A solution of Eq. (10) with boundary conditions (11) is sought in the form

$$n = \sum_{m=-2}^2 N_m(x, y) \exp[imk(ct - x)], N_{-m} = N_m^*, \quad (13)$$

in agreement with (1), and automatically satisfying the required condition of periodicity. It follows from general considerations and from Eqs. (1)-(3) (as well as being verified by the analysis below) that $N_m \sim q^{m/2}$. Substituting (13) into (10) and (11), and taking into account the expression for F in (1) and the fact that $|\Psi_1| \sim \sqrt{q}$, $|\Psi_0| \sim |\Psi_2| \sim q$, we obtain the following problem for finding the functions $N_m(x, y)$ with $m = 0, 1, 2$:

$$(1 + \Psi_0) \frac{\partial N_0}{\partial x} + \left(\frac{\partial N_{-1}}{\partial x} + iky \frac{\partial N_{-1}}{\partial y} + ikN_{-1} \right) \Psi_1 + \left(\frac{\partial N_1}{\partial x} - iky \frac{\partial N_1}{\partial y} - ikN_1 \right) \Psi_{-1} = \frac{\partial^2 N_0}{\partial y^2}, \quad (14)$$

$$N_0 = 0, y = 0; N_0 = 1, x = 0; N_0 \rightarrow 1, y \rightarrow \infty;$$

$$ibN_1 + (1 + \Psi_0) \frac{\partial N_1}{\partial x} + \left(\frac{\partial N_0}{\partial x} + iky \frac{\partial N_0}{\partial y} \right) \Psi_1 = \frac{\partial^2 N_1}{\partial y^2}, \quad (15)$$

$$N_1 = 0, y = 0; N_1 = 0, x = 0; N_1 \rightarrow 0, y \rightarrow \infty;$$

$$2ibN_2 + (1 + \Psi_0) \frac{\partial N_2}{\partial x} + \left(\frac{\partial N_0}{\partial x} + 2iky \frac{\partial N_0}{\partial y} \right) \Psi_2 + \left(\frac{\partial N_1}{\partial x} + ik y \frac{\partial N_1}{\partial y} - ikN_1 \right) \Psi_1 = \frac{\partial^2 N_2}{\partial y^2},$$

$$b = \left(\frac{2}{3}c - 1 \right) k,$$

$$N_2 = 0, y = 0; N_2 = 0, x = 0; N_2 \rightarrow 0, y \rightarrow \infty. \quad (16)$$

The problems for the quantities N_m with $m = -1, -2$ are obtained from (15) and (16), respectively, after applying the complex conjugate operation. It is convenient to use the asymptotic expansions

$$N_m \sim q^{m/2} \sum_{j=0}^{\infty} N_{mj}(x, y; q), \quad N_{mj}(x, y; q) \sim q^j. \quad (17)$$

The problems for the functions $N_{mj}(x, y; q)$ are obtained after substituting (17) into (14)-(16) and separating different order terms in powers of \sqrt{q} . Of primary interest is not the relative concentration field itself $n(t, x, y)$, but the field obtained from it by time averaging:

$$\langle n \rangle = \lim_{T \rightarrow \infty} \int_0^T n dt \sim \sum_{j=0}^{\infty} N_{0j}(x, y; q). \quad (18)$$

Therefore, we restrict ourselves below to determining the functions $N_{00}(x, y; q)$ and $N_{01}(x, y; q)$ only, which are required so as to find $\langle n \rangle$ accurately up to terms of order q , inclusive.

Including terms of order unity, from (14) and (17) we obtain the problem for N_{00}

$$\frac{\partial N_{00}}{\partial x} = \frac{\partial^2 N_{00}}{\partial y^2}, \quad N_{00} = 0 (y = 0), \quad N_{00} = 1 (x = 0, y \rightarrow \infty),$$

with the self-similar solution

$$N_{00} = \frac{1}{\sqrt{\pi}} \int_0^u \exp\left(-\frac{z^2}{4}\right) dz, \quad u = \frac{y}{\sqrt{x}}. \quad (19)$$

It is seen from (14) that in determining N_{01} it is first necessary to find N_{10} , for which we obtain from (15) and (17) the equation

$$\frac{\partial N_{10}}{\partial x} + ibN_{10} = \frac{\partial^2 N_{10}}{\partial y^2} - \frac{\Psi_1}{\sqrt{\pi}} \left(ik - \frac{1}{2x} \right) \frac{y}{\sqrt{x}} \exp\left(-\frac{y^2}{4x}\right)$$

and vanishing conditions of N_{10} at $y = 0$, $x = 0$, and $y \rightarrow \infty$. The solution of this problem can be represented in the form [23]

$$N_{10} = \frac{1}{2\sqrt{\pi}} \int_0^x \frac{\exp[-b(x-z)]}{\sqrt{x-z}} \int_0^\infty f(\zeta, z) \left\{ \exp\left[-\frac{(y-\zeta)^2}{4(x-z)}\right] - \exp\left[-\frac{(y+\zeta)^2}{4(x-z)}\right] \right\} d\zeta dz, \quad b = \left(\frac{2}{3}c - 1 \right) k,$$

$$f(\zeta, z) = \frac{\Psi_1 \zeta}{\sqrt{\pi} z} \left(ik - \frac{1}{2z} \right) \exp\left(-\frac{\zeta^2}{4z}\right).$$

Transforming this expression, we obtain

$$N_{10} = \frac{i\Psi_1}{\sqrt{\pi} b} \frac{y}{x^{3/2}} \left[\frac{k}{b} (e^{-ibx} + ibx - 1) - \frac{1}{2} (1 - e^{-ibx}) \right] \exp\left(-\frac{y^2}{4x}\right). \quad (20)$$

The problem for N_{01} is obtained from (15) and (17). We have the equation

$$\frac{\partial N_{01}}{\partial x} = \frac{\partial^2 N_{01}}{\partial y^2} - \frac{\partial N_{00}}{\partial x} \Psi_0 - \left(\frac{\partial N_{-10}}{\partial x} + ik y \frac{\partial N_{-10}}{\partial y} + ik N_{-10} \right) \Psi_1 - \left(\frac{\partial N_{10}}{\partial x} - ik y \frac{\partial N_{10}}{\partial x} - ik N_{10} \right) \Psi_{-1}$$

and the vanishing conditions of N_{01} at $y = 0$, $x = 0$, and $y \rightarrow \infty$. Substituting the expression for N_{10} from (20), we obtain a solution in the form

$$N_{01} = -\frac{1}{\sqrt{\pi}} \frac{y}{x^{3/2}} \left\{ -\frac{1}{2} \Psi_0 x + 2\Psi_1 \Psi_{-1} \left[-\frac{k}{2b} \left(1 + \frac{k}{b} \right) x + \right. \right.$$

TABLE 3. Coefficients α_m in Eq. (25) for Small Reynolds Numbers; I-IV) Same as in Table 1; the Approximate Error Does Not Exceed 5%

$\alpha=0$				$\alpha=\pi/4$			
I	II	III	IV	I	II	III	IV
1,1710	1,1561	1,1509	1,0915	1,1164	1,0918	1,0805	1,0263
0,2394	0,2277	0,2067	0,0961	0,1738	0,1397	0,1217	0,0393
0,0512	0,0773	0,0495	0,0117	0,0619	0,0559	0,0447	0,0191

TABLE 4. Coefficients α_m in Eq. (25) for Moderate Reynolds Numbers: I-IV) Same as in Table 2; the Approximation Error Does Not Exceed 5%

$\alpha=0$				$\alpha=\pi/4$			
I	II	III	IV	I	II	III	IV
1,4836	2,0720	3,0890	3,1126	1,4004	1,7272	1,8166	1,4806
0,6123	1,4362	2,9071	2,8185	0,4948	0,9137	0,9735	0,4821
0,1253	0,4306	1,0329	0,9539	0,0854	0,1957	0,1656	0,0391
0,0121	0,1006	0,2512	0,2203	0,0028	0,0255	0,0051	-0,0001
0,0109	0,0243	0,0214	0,0144	0,0076	0,0063	-0,0058	-0,0005

$$\begin{aligned}
 & + \frac{2}{b} \left(\frac{k}{b} + \frac{1}{2} \right)^2 \sin bx - \frac{3}{b^2} \left(\frac{k}{b} + \frac{1}{2} \right)^2 \frac{1 - \cos bx}{x} \Big] \exp \left(-\frac{y^2}{4x} \right) - \\
 & - \frac{1}{\sqrt{\pi}} \frac{y^3}{x^{7/2}} \Psi_1 \Psi_{-1} \left\{ \frac{1}{2} \left(\frac{k}{b} \right)^2 x^2 + \frac{1}{b^2} \left(\frac{k}{b} + \frac{1}{2} \right)^2 (1 - \cos bx) - \right. \\
 & \left. - \frac{k}{b^2} \left(\frac{k}{b} + \frac{1}{2} \right) x \sin bx \right\} \exp \left(-\frac{y^2}{4x} \right). \tag{21}
 \end{aligned}$$

Using relations (19)-(21) and the standard procedures of [23], one can similarly solve the problems for the remaining functions $N_{mj}(x, y; q)$.

We introduce the time average of the local mass flow to the free surface of the film, taking into account that with the accuracy adopted the normal derivative can be replaced by the derivative with respect to η . Using (18), (19), and (21), as well as the equality $\Psi_{-1} = \Psi_1^*$, we obtain after a simple calculation

$$\begin{aligned}
 j = \frac{Dc_*}{l} \frac{\partial \langle n \rangle}{\partial y} \Big|_{y=0} & = \frac{Dc_*}{l\sqrt{\pi x}} \left\{ 1 + \frac{1}{2} \Psi_0 + \frac{k}{b} \left(\frac{k}{b} + 1 \right) \Psi_1 \Psi_1^* + \right. \\
 & \left. + \frac{2}{bx} \left(\frac{k}{b} + \frac{1}{2} \right)^2 \left[-2 \sin bx + \frac{3}{bx} (1 - \cos bx) \right] \Psi_1 \Psi_1^* \right\}. \tag{22}
 \end{aligned}$$

This relation also makes it possible to determine the time average of the local Sherwood number for different portions of the film. Of practical interest is the Sherwood number for a film of length L as a whole. From (22) we have approximately

$$\begin{aligned}
 Sh & = \frac{1}{Dc_*} \int_0^L j d\xi = \frac{\lambda}{Dc_*} \int_0^{L/\lambda} j dx \approx Sh_0 \left[1 + \frac{1}{2} \Psi_0 + \frac{k}{b} \left(\frac{k}{b} + 1 \right) \Psi_1 \Psi_1^* \right], \\
 Sh_0 & = \left(\frac{6}{\pi} \frac{u_0 L}{D} \right)^{1/2} = \left(\frac{6}{\pi} \frac{L}{H} \right)^{1/2} Re^{1/3} Sc^{1/2}, H = \left(\frac{3\nu^2}{g \cos \alpha} \right)^{1/3}. \tag{23}
 \end{aligned}$$

Here we introduced the Sherwood number Sh_0 for a laminar nonwavy film, corresponding to the well-known Higby theory of permeation, and we also used the relation between u_0 and h_0 for such a film [22]. The approximate equality in (23) corresponds to retaining the dominant term of the integral, proportional to $(L/\lambda)^{1/2}$; the following (omitted) term is of order $(L/\lambda)^{-1/2}$.

Relations (23) along with (2) or (3) fully determine the effect of wave formation in the film on convective mass exchange. From a practical point of view the most important terms are those for which $Re \gg 10$. In this case we have, with account of (3),

$$\kappa = \frac{Sh}{Sh_0} = 1 + \frac{c}{3} \left[\frac{2(c-1)^2}{2c/3-1} - 1 \right] q. \quad (24)$$

Calculated κ values for stationary wave regimes with small and moderate Reynolds numbers are also given in Tables 1 and 2. The dependence of κ on Re, as given in (24), is illustrated in Fig. 1 for different Fi. Also given are the theoretical curves following from [12-15], as well as the experimental data in [10, 24-27]. It is seen that the assumed theoretical dependences agree poorly with experiment (an exception is the curve following from the model with mixing and restoration of the diffusional layer). At the same time the theory suggested in the present study is in satisfactory agreement with experiment. For $Re > 10-20$ it worsens somewhat, which is related to the breakdown in the assumption of weak nonlinearity for large Re, an assumption essential for the analysis in [22].

The theoretical results on mass exchange of thin films with the surrounding gas, being lower in comparison with experiment, are also characteristic of models in other studies. The only exception known to the authors is [28], where a problem similar to (10) and (11) was solved by the small parameter method, somewhat recalling the method of the present study, with fair agreement with the experimental results in [26]. However, no final equations of type (23) or (24) were obtained in [28]. Besides, to construct the theoretical dependences of the quantities characterizing the mass-exchange intensity on the physical and regime parameters it was necessary to use in [28] independently obtained experimental data on the practically realizable amplitude of film waves. To a large extent this is related to the absence of a sufficiently complete hydrodynamic description of stationary, weakly nonlinear wave regimes.

For applications it is usually desirable to have relatively simple approximate equations for calculating Sh (or κ). It seems that for deriving such equations it is most convenient to use the Chebyshev polynomials $T_m(s)$

$$T_{m+1} = 2s T_m - T_{m-1}, \quad T_0 = 1, \quad T_1 = s,$$

in whose terms these equations are

$$\kappa \approx \sum_{m=1}^M a_m T_{m-1}(s), \quad s = A Re + B, \quad (25)$$

$$A = 2(R_{\max} - 1)^{-1}, \quad B = -(R_{\max} + 1)(R_{\max} - 1)^{-1}.$$

For small Reynolds numbers, when relations (2) and Table 1 are valid, we took $R_{\max} = [Fi^{1/11}]$, $M = 3$; for moderate Reynolds numbers (relations (3) and Table 2) we took $R_{\max} = [6 Fi^{1/11}]$, $M = 5$. The values of the a_m coefficients in these cases are given in Tables 3 and 4.

In conclusion, we firstly note that, as follows from (22), the increase in width of the diffusional layer along the film is accompanied by its oscillations, which do not vanish even after time averaging. Secondly, the method suggested of solving the problem of convective diffusion, uniquely relating the mass-exchange characteristics with the characteristics of the wave flow regime, remains fully adequate if for any reason the theory in [22] is not valid (for example, in the presence of a tangential stress on the free surface due to a gas flow under conditions in which there exists a soluble or insoluble surface-active material). This method can also be applied without major difficulties to the analysis of more complex problems (for example, simultaneous heat and mass transfer with strong thermal sorption or desorption effects, and in the presence of evaporation or condensation on the free surface).

NOTATION

A, B, and a_i , coefficients introduced in (25); b, parameter in (20); c, dimensionless phase velocity of waves and the dimensionless admixture concentration; c_* , concentration far from the free surface; D, diffusion coefficient; F, function introduced in (1); H, parameter in (23); h and h_0 , film thickness in the wavy and nonwavy regimes; k, wave number; L, length of the mass exchange portion; l , characteristic width of the diffusion layer; M, order of the approximating polynomial; N_i , functions introduced in (13); n, dimensionless concentration; q, squared amplitude of the main harmonic of film thickness perturbation; R_{\max} , maximum value of the Reynolds number in the approximation; T_i , Chebyshev polynomials; t, dimensionless time; u_0 , mean velocity in the nonwavy regime; $v_x, v_y, v_z, v_n, v_s, v_t$, longitudinal and transverse components of the dimensional and dimensionless velocities; x and y, dimensionless

coordinates; α , angle between the planar sublayer of the film and the vertical; ϵ , long-wave parameter; ξ and η , dimensional coordinates; κ , Sherwood number ratio for the wavy and non-wavy regimes; λ , wavelength; ν , kinematic viscosity; ρ , liquid density; τ , dimensional time; φ , dimensionless wave amplitude; ψ , dimensionless velocity disturbance; Φ_i , Ψ_i , functions introduced in (1); Fi , film number; Re , Pe , Sc , and Sh , Reynolds, Peclet, Schmidt, and Sherwood numbers, respectively; We , Weber number; the angular and square brackets denote, respectively, time averaging and the integral part of a number; and the asterisk above stands for complex conjugate.

LITERATURE CITED

1. P. L. Kapitsa, "Wave flow of thin layers of a viscous liquid," *Zh. Eksp. Teor. Fiz.*, 18, No. 3, 3-28 (1948).
2. R. E. Emmert and R. L. Pigford, "A study of gas absorption in falling liquid films," *Chem. Eng. Progr.*, 50, No. 2, 87-93 (1954).
3. B. I. Konobeev, V. A. Malyusov, and N. M. Zhavoronkov, "Study of film absorption at high gas velocity," *Khim. Prom.*, No. 7, 475-481 (1961).
4. Yu. I. Dytner'skii and N. S. Brekhovskikh, "Several problems of CO₂ absorption by water during film flow," *Teor. Osn. Khim. Tekhnol.*, 2, 845-849 (1968).
5. I. A. Gil'denblat, A. L. Lashakov, S. A. Krashennnikov, and A. I. Rodinov, "Effect of the diffusion coefficient on mass transfer to a liquid film," *Teor. Osn. Khim. Tekhnol.*, 3, 305-307 (1969).
6. A. S. Gorshkov, P. A. Semenov, A. M. Tsirlin, and M. F. Galiullin, "Study of absorption of a slowly soluble gas in thin liquid layers," *Teor. Osn. Khim. Tekhnol.*, 3, 209-215 (1969).
7. R. A. Seban and A. Fagri, "Wave effects on the transport falling laminar liquid films," *Trans. ASME J. Heat Transfer*, 100, No. 1, 143-147 (1978).
8. A. P. Burdukov, N. S. Bufetov, and A. R. Dorokhov, "Absorption on a discharging liquid film," *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Tekh. Nauk*, 13, No. 3, 48-52 (1979).
9. V. E. Nakoryakov, A. P. Burdukov, N. S. Bufetov, N. I. Grigor'eva, and A. R. Dorokhov, "Heat and mass transfer in vertical wavy liquid films," in: *Heat and Mass Transfer-VI* [in Russian], Proc. 6th All-Union Conf. Heat and Mass Transfer, Vol. 4, Pt. 2, Minsk (1980), pp. 14-19.
10. V. E. Nakoryakov, B. P. Pokusaev, and S. V. Alekseenko, "Desorption of a weakly soluble gas from discharging wavy liquid films," in: *Calculation of Heat and Mass Transfer in Chemical Energy Processes* [in Russian], ITF SO Akad. Nauk SSSR, Novosibirsk (1981), pp. 23-36.
11. P. L. Kapitsa, "Thermal conductivity and diffusion in a liquid medium with periodic flow," *Zh. Eksp. Teor. Fiz.*, 21, 964-978 (1951).
12. V. G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, New Jersey (1962).
13. S. D. Bagaeva, P. A. Semenov, and M. F. Galiullin, "Diffusion during wave motion of thin liquid layer," *Teor. Osn. Khim. Tekhnol.*, 7, 504-511 (1973).
14. K. Javdani, "Mass transfer in wavy liquid films," *Chem. Eng. Sci.*, 29, No. 1, 61-69 (1974).
15. L. P. Kholpanov, B. Ya. Shkadov, V. A. Malyusov, and N. M. Zhavoronkov, "Mass exchange in a liquid film with wave formation," *Teor. Osn. Khim. Tekhnol.*, 1, No. 1, 73-79 (1967).
16. L. P. Kholpanov, B. Ya. Shkadov, V. A. Malyusov, and N. M. Zhavoronkov, "Study of hydrodynamics and mass exchange in a liquid film with account of input portions," *Teor. Osn. Khim. Tekhnol.*, 10, 659-669 (1976).
17. S. Portalski, "Eddy formation in film flow down a vertical plate," *Ind. Eng. Chem. Fundam.*, 3, No. 1, 49-53 (1964).
18. V. Penev, V. S. Krylov, Chr. Boyadjiev, and V. P. Vorotilin, "Wavy flow of thin liquid films," *Int. J. Heat Mass Transfer*, 15, 1395-1406 (1972).
19. F. Ho and R. Hummel, "Average velocity distributions within falling liquid films," *Chem. Eng. Sci.*, 25, 1225-1238 (1970).
20. V. E. Nakoryakov, B. G. Pokusaev, S. V. Alekseenko, and V. V. Orlov, "Instantaneous velocity profile in a wavy liquid film," *Inzh.-Fiz. Zh.*, 33, 399-405 (1977).
21. N. N. Kulov, M. Yu. Murav'ev, V. A. Malyusov, and N. M. Zhavoronkov, "Velocity profiles in discharging liquid films," *Teor. Osn. Khim. Tekhnol.*, 16, 499-509 (1982).
22. Yu. A. Buevich and S. V. Kudymov, "Weakly nonlinear stationary waves in a thin liquid film," *Inzh.-Fiz. Zh.*, 45, 566-576 (1983).

23. A. G. Butkovskii, Characteristics of Systems with Distributed Parameters [in Russian], Nauka, Moscow (1979).
24. N. N. Kulov and V. A. Malyusov, "Mass transfer in a tube with an irrigated wall during mixing of a liquid film," Teor. Osn. Khim. Tekhnol., 1, 213-223 (1967).
25. Yu. I. Dytner'skii and G. S. Borisov, "Study of mass exchange in the liquid phase," in: Chemical Technology Processes [in Russian], Nauka, Moscow-Leningrad (1965), pp. 266-270.
26. S. Kamei and J. Oishi, "Hold-up in wetted wall tower," Mem. Fac. Eng. Kyoto Univ., 18, No. 1, 1-12 (1956).
27. H. Hikita, "Mass-transfer coefficient and contacting efficiency between two phases," Preprint 25th Anniversary Congr., Soc. Chem. Eng. Jpn., 135-142 (1961).
28. E. Ruckenstein and C. Berbente, "Mass transfer to falling liquid films at low Reynolds numbers," Int. J. Heat Mass Transfer, 11, 743-753 (1968).

STRUCTURAL PROPERTIES OF SURFACE LAYERS OF DISPERSED SYSTEMS BY THE METHOD OF ESTIMATING THE DEFORMATIONS OF THE CRYSTAL LATTICE OF THE SOLID PHASE AND THE DENSITY OF THE DISPERSED MEDIUM. I

P. P. Olodovskii and L. A. Malkova

UDC 541.182.3

The distribution of the number of molecules of the dispersed medium in surface layers of the solid phase as a function of the concentration of water molecules, adsorbed on montmorillonite, is estimated.

The effect of adsorbed water and organic compounds on the change in the parameters and volume of the unit crystalline cell of kaolinite is demonstrated in [1, 2]. Calculations of the deformation of the lattice are performed.

In this work, the object of the investigation was the agrillaceous fraction of montmorillonite, separated from natural Crimean kill. The technique and the procedure used in the measurements remained essentially the same. The method of x-ray diffractometry using a DRON-2 was used.

Powder (3 g) was pressed into a special cell, whose reflecting surface was covered with beryllium foil, which was almost transparent to x rays. The moisture content of the sample was varied by drying in a vacuum dryer and by moistening with water in the dryer. Water vapor was added or removed through an opening in the cell, tightly covered with a threaded seal. The moisture content was determined by weighing.

The organic compounds used consisted of nitrobenzene and toluene. For adsorption of molecules of these compounds on the powder, the sample in the cell with an established moisture content was placed into the system with the air removed beforehand and saturated with nitrobenzene or toluene vapors.

A picture of the specimen in reflection was made in the discrete regime with Cu K_{α} radiation. The current in the tube was 16 mA, the voltage was 36 kV, and the gaps equal 0.5, 1, and 0.25 mm. The vertical divergence of the Soller slits was 1.5° . An N_i filter was used. The limit of the measurements was 1000 counts/sec, $R_c = 5$. The angle 2θ for specific moisture contents of montmorillonite was recorded on a digital printer from the maximum intensity of reflections with an error of $2\theta = 0.005^{\circ}$ (with a step size of 0.01°). The reflections at (220), (222), and (400) of cerium dioxide, which was mixed with montmorillonite in a ratio of 1:20, were used as standards.

The parameters and the volume of the crystal lattice were calculated from four reflections of montmorillonite (200), (005), (060), and (331) with the help of formulas for the monoclinic syngony and computer programs that we wrote in FORTRAN.

Central Scientific-Research Institute for Complex Utilization of Water Resources, Minvodkhoza SSSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 46, No. 5, pp. 746-754, May, 1984. Original article submitted February 3, 1983.