

## THEORY OF THE MECHANODIFFUSION TRANSFER OF MULTICOMPONENT LIQUIDS IN CROSS-LINKED ELASTOMERS

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**Introduction.** The mechanical processes of deformation and mass transfer in solids are interrelated. The introduction of a penetrant into a solid body is accompanied by the occurrence of internal stresses in the solid. The nonuniform stress field caused by external factors can affect the transfer process and lead to redistribution of the penetrant in the volume of the solid. Such phenomena are called mechanodiffusion and are described in theory on the basis of synthesis of the mechanics of a solid deformable body and diffusion theory.

At present, the theory of mechanodiffusion processes based on the linear theory of deformation has been developed most extensively [1]. However, it is inapplicable to cross-linked elastomers, because, under mechanical loading or interaction with organic solvents, the latter can undergo strain reaching hundreds of percent. The deformation processes and the interaction of mechanical and concentration fields in these systems are substantially nonlinear. Hence, they should be described using theoretical models that treat transfer processes against the background of arbitrary strains of an elastic matrix and take into account the physical nonlinearity of the mechanical and transport properties of the material.

The development of nonlinear models of mechanodiffusion is dictated by the necessity of describing simultaneous processes of deformation and mass transfer in hyperelastic polymers, for example, in the prediction of the longevity of elastomer-based articles working in physically aggressive media [2].

The general principles of developing nonlinear models of mass transfer in an elastically deformed matrix were developed in [3–5]. The extremely general formulation of constitutive relations and the use of nontraditional thermodynamic parameter such as partial stress tensors and diffusion forces lead to significant difficulties in attempts to apply the indicated theory to the description of specific objects [6, 7]. Probably, because of this, it is little used for the solution of applied problems.

In the present paper, a theory for mechanical diffusion processes in hyperelastic matrices is formulated in terms of the global stress tensor and chemical potentials. This theory is obtained from the dynamic theory of mixtures using a diffusion approximation. The approach described in [3–5] is used as the basis and is generalized to the case of a multicomponent mixture. An important feature of the present work is that, owing to the structure of equations and constitutive relations, the general model can be used without difficulty to describe specific systems.

**1. Basic Definitions and Notation.** We study a homogeneous, isotropic, elastic matrix and an  $N$ -component liquid dissolved in it. This system is called a mixture. The mixture components are numbered by Latin letters, and  $N + 1$  corresponds to the matrix. We introduce the following notation:  $\rho_a$  are the partial densities,  $n_a$  are the molar concentrations,  $\varphi_a$  are the volume fractions,  $\mathbf{v}_a$  are the motion velocities of the mixture components,  $V_a$  and  $M_a$  are the volume and mass of 1 mole of the  $a$ th component,  $\psi$ ,  $U$ , and  $s$  are the free energy, internal energy, and entropy of the unit mass of the mixture,  $T$  and  $\rho$  are the absolute temperature and density of the mixture, and  $f$  is the density of the free energy of the mixture. Obviously, the relations

$$\rho_a = M_a n_a, \quad \rho = \sum_{a=1}^{N+1} \rho_a, \quad f = \rho \psi \quad (1.1)$$

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are valid.

The diffusion velocities  $\mathbf{u}_a$  and the diffusion fluxes  $\mathbf{j}_a$  are given relative to the elastic matrix by the formulas

$$\mathbf{u}_a = \mathbf{v}_a - \mathbf{v}_{N+1}, \quad \mathbf{j}_a = n_a \mathbf{u}_a \quad (a = 1, \dots, N). \quad (1.2)$$

In the description of the strain-stress state of the polymeric matrix in the present work, we use the system of notions and the form of representation of the relations of nonlinear elastic theory and tensor analysis presented in [8]. They are briefly outlined below.

In the mechanics of a solid deformable solid, it is customary to use body coordinates. To define this system, we choose a certain fixed configuration of the mixture, introduce the coordinate system  $q^k$  ( $k = 1, 2, 3$ ) and relate it to the elastic matrix. The location of particles of the matrix in this configuration, called the reference configuration, is given by the radius vectors

$$\mathbf{r} = \mathbf{r}(q^1, q^2, q^3). \quad (1.3)$$

The motion of the matrix is described by the radius vector

$$\mathbf{R} = \mathbf{R}(q^1, q^2, q^3, t). \quad (1.4)$$

This function gives the actual configuration of the matrix. We determine the substantial derivatives with respect to time for each of the components

$$\frac{D^{(a)}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_a \cdot \nabla, \quad a = 1, \dots, N+1 \quad (1.5)$$

and the derivative related to the motion of the centers of mass of the elementary volumes of the mixture:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla, \quad (1.6)$$

where  $\mathbf{v} = \sum_{a=1}^{N+1} \mathbf{v}_a (\rho_a / \rho)$  is the mass average velocity of the elementary volume. Here and below, unless otherwise specified,  $\partial/\partial t$  denotes a partial derivative with respect to time at a fixed point in real space. The substantial derivative associated with the matrix is denoted by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}_{N+1} \cdot \nabla. \quad (1.7)$$

The vector basis

$$\mathbf{r}_k = \frac{\partial \mathbf{r}}{\partial q^k}, \quad \mathbf{R}_k = \frac{\partial \mathbf{R}}{\partial q^k} \quad (1.8)$$

and the gradient operators

$$\nabla^0 = \mathbf{r}^k \frac{\partial}{\partial q^k}, \quad \nabla = \mathbf{R}^k \frac{\partial}{\partial q^k} \quad (1.9)$$

are defined in the reference and actual configurations.

The strains of the matrix are described using the strain gradient  $\mathbf{Q}$  and the Finger measure  $\mathbf{F}$ , which are second-order tensors:

$$\mathbf{Q} = \nabla^0 \mathbf{R}, \quad \mathbf{F} = \mathbf{Q}^t \cdot \mathbf{Q}. \quad (1.10)$$

The tensor  $\mathbf{F}$  is symmetric and has three independent invariants:

$$I_1(\mathbf{F}) = \mathbf{E} \cdot \mathbf{F}, \quad I_2(\mathbf{F}) = (I_1^2(\mathbf{F}) - I_1(\mathbf{F}^2))/2, \quad I_3(\mathbf{F}) = \det \mathbf{F}, \quad (1.11)$$

Here  $\mathbf{E}$  is a unit tensor.

In what follows, we need the formulas of differentiation of the invariants of the Finger measure [8],

$$\frac{\partial I_1}{\partial \mathbf{Q}} = 2\mathbf{Q}, \quad \frac{\partial I_2}{\partial \mathbf{Q}} = 2\mathbf{Q} \cdot (\mathbf{E}I_1 - \mathbf{F}), \quad \frac{\partial I_3}{\partial \mathbf{Q}} = 2I_3(\mathbf{Q}^t)^{-1}, \quad (1.12)$$

and the relation between the parameters of an oriented surface element in the actual configuration  $dO$  and its prototype in the reference configuration  $do$ :

$$\mathbf{n}do = I_3^{-1/2} \mathbf{Q} \cdot \mathbf{N}dO. \quad (1.13)$$

Here  $\mathbf{n}$  and  $\mathbf{N}$  are unit normal vectors that give the orientation of surface elements in the reference and actual configurations, respectively.

**2. Basic Equations and Constitutive Relations of the Nonlinear Theory of Mechanodiffusion.** According to [3–5], we shall use the partial equations of mass balance and pulse for each component of the mixture and the general mass balance equation:

$$\frac{\partial \rho_a}{\partial t} + \nabla \cdot (\rho_a \mathbf{v}_a) = 0, \quad a = 1, \dots, N + 1; \quad (2.1)$$

$$\rho_a \frac{D^{(a)}}{Dt} \mathbf{v}_a = \nabla \cdot \boldsymbol{\sigma}_a + \mathbf{p}_a, \quad a = 1, \dots, N + 1; \quad (2.2)$$

$$\rho \frac{DU}{Dt} + \sum_{a=1}^{N+1} (\mathbf{p}_a \cdot \mathbf{v}_a - \boldsymbol{\sigma}_a \cdot \nabla \mathbf{v}_a^t) + \nabla \cdot \mathbf{q} - r = 0. \quad (2.3)$$

Here  $\boldsymbol{\sigma}_a$  are the partial tensors of Cauchy–Green stresses,  $\mathbf{p}_a$  is the force of interaction between the  $a$ th component and the mixture,  $\mathbf{q}$  is the heat-flux density, and  $r$  is the density of internal heat sources. The forces  $\mathbf{p}_a$  are internal, and, hence,

$$\sum_{a=1}^{N+1} \mathbf{p}_a = 0. \quad (2.4)$$

The second law of thermodynamics is written as the dissipative Clausius–Duhem inequality [3–5]:

$$\rho T \frac{Ds}{Dt} - r + \nabla \cdot \mathbf{q} - (\mathbf{q} \cdot \nabla T)/T \geq 0.$$

Using (2.3) and (2.4) and the definition of the diffusion velocities (1.2), we represent the above relation in terms of the free energy  $\psi = U - Ts$ :

$$\rho \frac{D\psi}{Dt} + \rho s \frac{DT}{Dt} + \frac{\mathbf{q} \cdot \nabla T}{T} + \sum_{a=1}^N \mathbf{p}_a \cdot \mathbf{u}_a - \sum_{a=1}^{N+1} \boldsymbol{\sigma}_a \cdot \nabla \mathbf{v}_a^t \leq 0. \quad (2.5)$$

The constitutive equations of the system considered are modeled by the following relations:

$$\psi = \psi(\mathbf{Q}, \rho_1, \dots, \rho_N, T); \quad (2.6)$$

$$\boldsymbol{\sigma}_a = \boldsymbol{\sigma}_a(\mathbf{Q}, \rho_1, \dots, \rho_N, T), \quad a = 1, \dots, N + 1; \quad (2.7)$$

$$\mathbf{p}_a = \mathbf{p}_a(\mathbf{Q}, \rho_1, \dots, \rho_N, T, \mathbf{u}_1, \dots, \mathbf{u}_N), \quad a = 1, \dots, N. \quad (2.8)$$

The absence of velocity gradients among the arguments of relations (2.7) and (2.8) means that we ignore the viscosity of the mixture components.

Taking into account relations (2.6) in the dissipative inequality (2.5), we obtain

$$\begin{aligned} & \rho \left( \frac{\partial \psi}{\partial T} + s \right) \frac{DT}{Dt} - \sum_{a=1}^N \left( \boldsymbol{\sigma}_a + \rho \rho_a \frac{\partial \psi}{\partial \rho_a} \mathbf{E} \right) \cdot \nabla \mathbf{v}_a^t + \left( \rho \mathbf{Q}^t \frac{\partial \psi}{\partial \mathbf{Q}} - \boldsymbol{\sigma}_{N+1} \right) \cdot \nabla \mathbf{v}_{N+1}^t \\ & + \sum_{a=1}^N \left( \mathbf{p}_a + \rho_a \nabla \mathbf{Q}^t \cdot \frac{\partial \psi}{\partial \mathbf{Q}} - \rho \frac{\partial \psi}{\partial \rho_a} \nabla \rho_a + \rho_a \sum_{b=1}^N \frac{\partial \psi}{\partial \rho_b} \nabla \rho_b \right) \cdot \mathbf{u}_a + \frac{\mathbf{q} \cdot \nabla T}{T} \leq 0. \end{aligned}$$

Restricting our consideration to mechanodiffusion processes under isothermal conditions

$$T = \text{const}, \quad \nabla T = 0 \quad (2.9)$$

and applying familiar methods of analysis [5] to the last inequality, we arrive at the conclusion that, on the assumptions made above (2.6)–(2.9), the necessary and sufficient condition for satisfaction of this inequality

in arbitrary processes is the validity of the relations

$$s = -\frac{\partial\psi}{\partial T}; \quad (2.10)$$

$$\sigma_a = -\rho_a \rho \mathbf{E} \frac{\partial\psi}{\partial \rho_a}, \quad a = 1, \dots, N; \quad (2.11)$$

$$\sigma_{N+1} = \rho \mathbf{Q}^t \cdot \frac{\partial\psi}{\partial \mathbf{Q}}; \quad (2.12)$$

$$\mathbf{p}_a^E = -\rho_a \nabla \mathbf{Q}^t \cdot \frac{\partial\psi}{\partial \mathbf{Q}} + \rho \frac{\partial\psi}{\partial \rho_a} \nabla \rho_a - \rho_a \sum_{b=1}^N \frac{\partial\psi}{\partial \rho_b} \nabla \rho_b; \quad (2.13)$$

$$\sum_{a=1}^N \mathbf{p}_a^D \cdot \mathbf{u}_a \leq 0, \quad (2.14)$$

where  $\mathbf{p}_a^E$  and  $\mathbf{p}_a^D$  are, respectively, the equilibrium and dissipative components of the force  $\mathbf{p}_a$ , which are given by the formulas

$$\mathbf{p}_a^E = \mathbf{p}_a(\mathbf{Q}, \rho_1, \dots, \rho_N, 0, \dots, 0); \quad (2.15)$$

$$\mathbf{p}_a = \mathbf{p}_a^E + \mathbf{p}_a^D. \quad (2.16)$$

Here and below, by virtue of (2.9), the temperature dependence is omitted.

We make the following assumptions. First, we assume that the transfer and loading processes of the elastic matrix proceed so slowly that the accelerations in the equations of motion (2.2) can be ignored and set equal to zero:

$$D^{(a)} \mathbf{v}_a / Dt = 0. \quad (2.17)$$

Second, the resistance forces acting on the liquid components in the mixture are modeled by the following relations, which are linear in diffusion fluxes:

$$\mathbf{p}_a^D = -\sum_{b=1}^N n_a \mathbf{L}_{ab} \cdot \mathbf{j}_b. \quad (2.18)$$

Here the coefficients  $\mathbf{L}_{ab}$  are second-order tensors and functions of the form

$$\mathbf{L}_{ab} = \mathbf{L}_{ab}(\mathbf{Q}, n_1, \dots, n_N), \quad a, b = 1, \dots, N. \quad (2.19)$$

Inequality (2.14) and Eqs. (2.2) with allowance for (2.16)–(2.18) are written as

$$\sum_{a,b=1}^N \mathbf{j}_a \cdot \mathbf{L}_{ab} \cdot \mathbf{j}_b \geq 0; \quad (2.20)$$

$$\sum_{b=1}^N \mathbf{L}_{ab} \cdot \mathbf{j}_b = \nabla \cdot \sigma_a + \mathbf{p}_a^E, \quad a = 1, \dots, N. \quad (2.21)$$

It follows from relation (2.20) that the coefficients  $\mathbf{L}_{ab}$  form a nonnegatively defined matrix.

The next step is the passage from the partial stress tensors  $\sigma_a$  and the diffusion forces  $\mathbf{p}_a^E$  to the chemical potentials and the global stress tensor, which are expressed most simply in terms of the free-energy density of the mixture (1.1) if the latter is treated as a function of the form

$$f = f(\mathbf{Q}, n_1, \dots, n_{N+1}). \quad (2.22)$$

Here the arguments include the concentration of the matrix material  $n_{N+1}$ , which is not an independent variable. As shown later, it is related to the strains of the matrix by formula (2.39). It is not hard to see that, with allowance for this relationship, formula (2.22) is equivalent to (2.6). By virtue of representation (2.22),

we can consider the free energy as a homogeneous first-order function of the variables  $n_a$  ( $a = 1, \dots, N + 1$ ) and use the Euler theorem:

$$\sum_{a=1}^{N+1} n_a \frac{\partial f}{\partial n_a} = f. \quad (2.23)$$

Summing up Eqs. (2.2) with allowance for (2.4) and (2.17), we obtain the following equation of mechanical equilibrium for the mixture:

$$\nabla \cdot \boldsymbol{\sigma} = 0. \quad (2.24)$$

Here  $\boldsymbol{\sigma} = \sum_{a=1}^{N+1} \boldsymbol{\sigma}_a$  is the global Cauchy–Green stress tensor. Summing up relations (2.11) and (2.12) and transforming them with allowance for (2.22), (2.23), and (2.39), we write the following expression for  $\boldsymbol{\sigma}$  in terms of the free-energy density:

$$\boldsymbol{\sigma} = \mathbf{Q}^t \cdot \frac{\partial f}{\partial \mathbf{Q}}. \quad (2.25)$$

Note that differentiation here is performed for fixed  $n_a$  ( $a = 1, \dots, N + 1$ ).

Using relations (2.11) and (2.13), we bring the right side of Eqs. (2.21) to the form

$$\nabla \cdot \boldsymbol{\sigma}_a + \mathbf{p}_a^E = -n_a \nabla \mu_a, \quad a = 1, \dots, N, \quad (2.26)$$

where the quantities

$$\mu_a = \frac{\partial f}{\partial n_a} \quad (2.27)$$

have the meaning of the chemical potentials of the mixture components.

Substituting (2.26) into (2.21), we obtain the following equations that relate diffusion fluxes to the chemical-potentials gradients:

$$\sum_{b=1}^N \mathbf{L}_{ab} \cdot \mathbf{j}_b = -\nabla \mu_a, \quad a = 1, \dots, N. \quad (2.28)$$

Using the definition of diffusion fluxes (1.2), the relation between the molar and mass concentrations (1.1), and the definition of the derivative (1.7), we write the balance equations (2.1) as

$$\frac{dn_a}{dt} + n_a \nabla \cdot \mathbf{v}_{N+1} = -\nabla \cdot \mathbf{j}_a, \quad a = 1, \dots, N; \quad (2.29)$$

$$\frac{dn_{N+1}}{dt} + n_{N+1} \nabla \cdot \mathbf{v}_{N+1} = 0. \quad (2.30)$$

Equations (2.24) and (2.27)–(2.30) and the constitutive relations (2.19), (2.20), (2.22), and (2.25) are the basic relations for the system considered. They describe the joint deformation and mass-transfer processes in the elastic matrix under isothermal conditions. These equations describe the mechanodiffusion process in the actual configuration, which, as a rule, is not known beforehand and is to be determined. In some cases, the mathematical description of the process is markedly simplified if all equations are formulated in the reference configuration. This is achieved by applying familiar transformations to the initial system of equations [8]. The result of these transformations is

$$\frac{\partial n_a^0}{\partial t} = -\nabla^0 \cdot \mathbf{j}_a^0, \quad a = 1, \dots, N; \quad (2.31)$$

$$\frac{\partial n_{N+1}^0}{\partial t} = 0; \quad (2.32)$$

$$\sum_{b=1}^N \mathbf{L}_{ab}^0 \cdot \mathbf{j}_b^0 = -\nabla^0 \mu_a; \quad (2.33)$$

$$\nabla^0 \cdot \boldsymbol{\sigma}^0 = 0. \quad (2.34)$$

Here it is assumed that all quantities that enter into the equations are functions of body coordinates, and the partial derivatives with respect to times are taken for fixed  $q^i$ , and, hence, they are equivalent to the substantial derivative (1.7). The parameters that enter into the equations are defined by the formulas

$$n_a^0 = I_3^{1/2} n_a; \quad (2.35)$$

$$\sigma^0 = I_3^{1/2} (\mathbf{Q}^{-1})^t \cdot \sigma; \quad (2.36)$$

$$\mathbf{j}_a^0 = I_3^{1/2} (\mathbf{Q}^{-1})^t \cdot \mathbf{j}_a; \quad (2.37)$$

$$\mathbf{L}_{ab}^0 = I_3^{-1/2} \mathbf{Q} \cdot \mathbf{L}_{ab} \cdot \mathbf{Q}^t. \quad (2.38)$$

The quantities  $n_a^0$  are numerically equal to the number of moles of the  $a$ th component in the unit volume of the reference configuration of the mixture. The tensor  $\sigma^0$  is called the Piola stress tensor [8]. By analogy, the fluxes  $\mathbf{j}_a^0$  can be called the Piola diffusion fluxes.

Note that relations (2.32) and (2.35) lead to the following relation for the concentration of the matrix material:

$$n_{N+1} = I_3^{-1/2} n_{N+1}^0. \quad (2.39)$$

Here, by virtue of (2.32),  $n_{N+1}^0$  is a constant and depends only on the choice of the reference configuration.

The constitutive relations (2.19), (2.22), (2.25), and (2.27) are of the general character, but they can be specified using the objectivity principle [8] and taking into account the isotropy property of an elastic matrix. As is known, the free energy of an isotropic material can be represented as a function of the invariants of the strain measure if the following undistorted configuration is used as the reference configuration [8]:

$$f = f(I_1, I_2, I_3, n_1, \dots, n_{N+1}). \quad (2.40)$$

In the case of a mixture, there is a set of such undistorted configurations, each of which is characterized by a uniform distribution of the liquid over the matrix volume and by the absence of external mechanical loads. Each of these configurations can be used as the reference configuration, but the constitutive relations explicitly depend on the choice of the reference configuration. In reality, however, the physicomaterial properties of the material must not depend on such a choice. Hence, there must be a representation of the constitutive relations that is invariant with respect to the choice of the reference configuration. This representation is obtained by appropriate parametrization of all constitutive relations. Below, we propose one of the possible methods of such parametrization.

We define a new strain measure  $\hat{\mathbf{F}}$  and scalar parameters  $\Gamma_i$  by the formulas

$$\hat{\mathbf{F}} = \mathbf{F}/I_3^{1/3}; \quad (2.41)$$

$$\Gamma_1 = I_1(\hat{\mathbf{F}}) = I_1/I_3^{1/3}, \quad \Gamma_2 = I_2(\hat{\mathbf{F}}) = I_2/I_3^{2/3}, \quad \Gamma_3 = I_3^{1/2} W/W_0, \quad (2.42)$$

where  $W = V_0/V$  is the ratio of the volume of the dry polymer  $V_0$  to the volume of the swollen polymer  $V$  in the unstressed state, and  $W_0$  is the value of  $W$  in the reference configuration. Obviously,  $W$  is a function of the mixture ratio:

$$W = W(n_1, \dots, n_N). \quad (2.43)$$

It follows from the definitions (2.41) and (2.42) that the strain measure  $\hat{\mathbf{F}}$  and the parameters  $\Gamma_1$  and  $\Gamma_2$  are insensitive to volume variations in the mixture, and  $\Gamma_3$  is sensitive only to those volume variations that are caused by mechanical loading. Svistkov [9] showed that the representation of the free energy in the form

$$f = f(\Gamma_1, \Gamma_2, \Gamma_3, n_1, \dots, n_{N+1}) \quad (2.44)$$

satisfies automatically the condition that the thermodynamic properties of the polymer be independent of the choice of the reference configuration. In this case, this parametrization allows one to write all constitutive relations in explicitly invariant form with respect to the reference configuration.

From (1.12), (2.25), (2.41), (2.42), and (2.44) for the Cauchy–Green tensor it follows that

$$\boldsymbol{\sigma} = \xi_1 \left( \hat{\mathbf{F}} - \frac{1}{3} \Gamma_1 \mathbf{E} \right) + \xi_2 \left( \hat{\mathbf{F}}^2 - \frac{1}{3} I_1(\hat{\mathbf{F}}^2) \mathbf{E} \right) - p \mathbf{E}; \quad (2.45)$$

$$\xi_1 = 2 \left( \frac{\partial f}{\partial \Gamma_1} + \Gamma_1 \frac{\partial f}{\partial \Gamma_2} \right), \quad \xi_2 = -2 \frac{\partial f}{\partial \Gamma_2}; \quad (2.46)$$

$$p = -\Gamma_3 \frac{\partial f}{\partial \Gamma_3}. \quad (2.47)$$

The derivation of (2.45) is similar to the derivation of a similar expression in [8], and, therefore, is not given herein.

Note that the parameter  $p$  has the meaning of pressure, as follows from the relation  $I_1(\boldsymbol{\sigma}) = -3p$ , to which relation (2.45) satisfies.

We obtain a formula for the chemical potentials of the mixture components by applying formulas (2.27) to (2.44). With allowance for (2.47), we have

$$\mu_a = \frac{\partial f}{\partial n_a} + V_a p, \quad a = 1, \dots, N; \quad (2.48)$$

$$V_a = W^{-1} \frac{\partial W}{\partial n_a}. \quad (2.49)$$

By virtue of the principle of material indifference and the isotropic property of the polymeric matrix, the tensor function (2.19) is representable in the form

$$\mathbf{L}_{ab} = l_{ab}^{(0)} \mathbf{E} + l_{ab}^{(1)} \hat{\mathbf{F}} + l_{ab}^{(2)} \hat{\mathbf{F}}^2, \quad (2.50)$$

where the coefficients  $l_{ab}^{(s)}$  are the scalar functions

$$l_{ab}^{(s)} = l_{ab}^{(s)}(\Gamma_1, \Gamma_2, \Gamma_3, n_1, \dots, n_N), \quad s = 0, 1, 2. \quad (2.51)$$

Equations (2.24), (2.28)–(2.30), and (2.43)–(2.51) form a closed system and model mechanodiffusion processes in isotropic elastomers for arbitrary deformations of the polymer matrix under quasi-static loading conditions. The constitutive relations in this case “are not related” to any reference configuration, which depends on the liquid distribution in the material.

In mechanics, elastomers are often regarded as incompressible materials, and this is quite justified in the description of mechanodiffusion processes. The condition of incompressibility of the mixture is of the form

$$\Gamma_3 = 1. \quad (2.52)$$

All equations and constitutive relations, except for (2.47), remain valid but are no longer dependent on  $\Gamma_3$ . As to the pressure, it lost the meaning of a thermodynamic parameter and is a free parameter that is determined by solution of the full system of equations subject to condition (2.52). This follows from the general principles for describing incompressible materials [8].

**3. On the Formulation of Boundary-Value Problems of Nonlinear Mechanodiffusion.** We consider a mechanodiffusion process in a bounded polymer body. It is completely described by function (1.4), which gives the actual configuration of the polymer matrix, and by the functions

$$n_a = n_a(q^1, q^2, q^3, t), \quad a = 1, \dots, N,$$

which determine the current distribution of liquid components in the polymer matrix. These functions are solutions of a certain boundary-value problem for system (2.24) and (2.28)–(2.30).

The formulation of the boundary-value problems of mechanodiffusion includes the specification of the reference and initial configurations of the mixture and the formulation of boundary conditions for the equations of mechanical equilibrium and transfer. The reference configuration should be undistorted, because relations (2.44)–(2.51) are valid only in this case. The reference configuration is given by relation (1.3) and the concentrations of the mixture components  $n_a^{(0)}$ , which are constant and do not depend on the coordinates.

The initial configuration is defined by the relations

$$\mathbf{R}(q^1, q^2, q^3, 0) = \mathbf{R}_0(q^1, q^2, q^3), \quad n_a(q^1, q^2, q^3, 0) = n_{0a}(q^1, q^2, q^3),$$

where the functions  $\mathbf{R}_0$  and  $n_{0a}$  define the configuration of the polymer matrix and the distribution of the mixture components at the initial time. If the initial configuration of the mixture is undistorted, it can be used as the reference configuration. In this case,  $\mathbf{R}_0 = \mathbf{r}(q^1, q^2, q^3)$  and  $n_{0a} = n_a^{(0)}$ .

The formulation of boundary conditions for the equation of mechanical equilibrium (2.24) does not differ fundamentally from the formulation of boundary-value problems in the nonlinear theory of elasticity [8]. Therefore, we turn to the formulation of boundary conditions for transfer equations. In diffusion theory, they are defined by specifying boundary concentrations of the diffusants (conditions of the first kind) and their gradients (conditions of the second kind). The remaining types of conditions are their combinations. These conditions follow from the assumption of thermodynamic equilibrium or equality of diffusion fluxes on the boundary of the contact of the body considered with the ambient medium or other bodies. Since, in liquids, gases, and undeformable bodies, the chemical potentials of diffusing components depend only on the concentrations (under isothermal conditions), the specification of chemical potentials on the contact boundary is equivalent to the specification of boundary conditions. For the same reason, the specification of fluxes on the boundary is equivalent to the specification of concentration gradients. This circumstance permits one to eliminate the chemical potentials of diffusants from consideration. In our case, the chemical potentials depend on the strain of the polymer matrix, and, hence, the boundary concentrations and their gradients turn out to be functions of time that are unknown beforehand even at fixed parameters of the ambient medium. An example is the free swelling of an elastomer in a liquid. It follows from this reasoning that, in the nonlinear theory of mechanodiffusion, it is more natural from a physical viewpoint to formulate the boundary conditions in terms of the chemical potential.

Thus, the boundary conditions of the first kind for the transfer equations are a system of the form

$$\mu_a(\Gamma_1, \Gamma_2, \Gamma_3, n_1, \dots, n_N) = \mu_a^*(q^1, q^2, q^3, t), \quad a = 1, \dots, N, \quad (3.1)$$

where the arguments of the chemical potentials on the left side are equal to the boundary values of the corresponding parameters and  $\mu_a^*$  are given functions of the body coordinates and time, defined on the surface of the body. If the polymer body contacts a liquid of fixed composition, these functions are equal to the chemical potentials of the liquid-phase components and are constants. Equations (3.1) relate the boundary concentrations of the liquid components to external conditions and strains of the polymer matrix

Boundary conditions of the second kind are formulated on the assumption that the normal constituents of the diffusion fluxes  $J_a$  on the boundary of the body in the reference configuration are given functions:

$$\mathbf{n} \cdot \mathbf{j}_a^0 = J_a(q^1, q^2, q^3, t), \quad a = 1, 2, \dots, N. \quad (3.2)$$

Here  $\mathbf{n}$  is the unit vector of the outer normal in the reference configuration and  $\mathbf{j}_a^0$  are the boundary values of the density vectors of the Piola diffusion fluxes. Using formulas (1.13) and (2.37), we come to the representation of conditions (3.2) in the actual configuration:

$$\mathbf{N} \cdot \mathbf{j}_a = J_a(\mathbf{N} \cdot \mathbf{F} \cdot \mathbf{N})^{1/2} I_3^{-1/2}. \quad (3.3)$$

Solving the system of linear equations (2.28) for the fluxes and using relations (3.3), we can express the chemical-potential gradients on the boundary of the body in terms of the known functions  $J_a$ .

Note that the boundary conditions (3.3) are similar to the corresponding conditions for the mechanical-equilibrium equation, which are used to describe the so-called dead loading [8].

**4. Equations and Constitutive Relations of One-Component Mechanodiffusion in Elastomers.** Let us consider the case of mechanodiffusion processes in cross-linked elastomers with the participation of an individual solvent (plasticizer). We formulate the transfer equations. For this, we turn to Eqs. (2.28), of which only one remains in the given case. Solving it with respect to the diffusion flux, we obtain

$$\mathbf{j} = -\mathbf{K} \cdot \nabla \mu, \quad (4.1)$$



where the second-order tensor is  $\mathbf{K} = \mathbf{L}_{11}^{-1}$ . For an isotropic elastomer, we have

$$\mathbf{K} = k_0 \mathbf{E} + k_1 \hat{\mathbf{F}} + k_2 \hat{\mathbf{F}}^2. \quad (4.2)$$

We assume that the mixture is incompressible, and, hence, the scalar functions  $k_s$  do not depend on  $\Gamma_3$ :

$$k_s = k_s(\Gamma_1, \Gamma_2, n_1), \quad s = 0, 1, 2. \quad (4.3)$$

By virtue of (4.1), we write the transfer equations in the form

$$\frac{dn_1}{dt} + n_1 \nabla \cdot \mathbf{v}_2 = \nabla \cdot (\mathbf{K} \cdot \nabla \mu), \quad \frac{dn_2}{dt} + n_2 \nabla \cdot \mathbf{v}_2 = 0. \quad (4.4)$$

In the reference configuration, these equations are of the form

$$\frac{\partial n_1^0}{\partial t} = \nabla^0 \cdot (\mathbf{K}^0 \cdot \nabla^0 \mu), \quad \frac{\partial n_2^0}{\partial t} = 0, \quad (4.5)$$

where

$$\mathbf{K}^0 = I_3^{1/2} (\mathbf{Q}^t)^{-1} \cdot \mathbf{K} \cdot \mathbf{Q}^{-1}. \quad (4.6)$$

In the Flory theory, it is assumed that the volumes of the mixture components are additive, and, hence,  $W = \varphi_2$ , and the incompressibility condition (2.52) reduces to the relation

$$I_3^{1/2} \varphi_2 / \varphi_2^0 = 1. \quad (4.7)$$

Note that from the second equation of (4.5) follows

$$\varphi_2^0 = \text{const}. \quad (4.8)$$

To obtain constitutive relations for the stress tensor and the chemical potential, it is necessary to specify the free energy. According to the Flory network theory [10], we write the free energy as

$$f = RT(n_1 \ln \varphi_1 + n_2 B \ln \varphi_2 + \chi \varphi_2 n_1 + AI_1 n_2 / 2). \quad (4.9)$$

Here  $\varphi_1$  and  $\varphi_2$  are the volume fractions of the liquid and the polymer, respectively ( $\varphi_1 + \varphi_2 = 1$ ),  $\chi$  is the Flory-Huggins interaction parameter,  $A$  and  $B$  are dimensionless parameters, and  $R$  is the universal gas constant. The latter term describes the elastic response of the polymer network, and the undistorted state of the dry polymer is the reference configuration, i.e.,  $\varphi_2^0 = 1$ . From this and condition (4.7) we obtain

$$I_3 = \varphi_2^{-2}. \quad (4.10)$$

We divide and multiply the latter term in (4.9) by  $I_3^{1/3}$ . Using the first formula of (2.42) and relation (4.10), we obtain an expression for the free energy in a form that is independent of the choice of the reference configuration:

$$f = RT(n_1 \ln \varphi_1 + n_2 B \ln \varphi_2 + \chi \varphi_2 n_1 + A \varphi_2^{-2/3} \Gamma_1 n_2 / 2).$$

From this formula and formulas (2.45), (2.46), and (2.48) for the chemical potential and the Cauchy-Green stress tensor it follows that

$$\mu = RT \left( \ln \varphi_1 + (1 - BZ^{-1}) \varphi_2 + \chi \varphi_2^2 + \frac{A}{3Z} \varphi_2^{1/3} \Gamma_1 \right) + pV_1; \quad (4.11)$$

$$\boldsymbol{\sigma} = C \varphi_2^{1/3} \left( \hat{\mathbf{F}} - \frac{1}{3} \Gamma_1 \mathbf{E} \right) - p \mathbf{E}, \quad (4.12)$$

where  $Z = V_2/V_1$  and  $C = ARTV_2^{-1}$ . Note that, by virtue of the assumption of incompressibility of the mixture, the pressure in these formulas is not a thermodynamic parameter but a connectivity parameter, which is generally determined by solution of the full system of equations subject to the incompressibility condition.

Using formula (2.36) to relation (4.12) and taking into account (4.7), for the Piola stress tensor we have

$$\sigma^0 = C(\varphi_2^0)^{1/3} \left( \mathbf{Q} - \frac{1}{3} I_1 (\mathbf{Q}^t)^{-1} \right) - p(\mathbf{Q}^t)^{-1} I_3^{1/2}. \quad (4.13)$$

The physical components of this tensor in the principal axes are

$$\sigma_k^0 = C(\varphi_2^0)^{1/3} \left( \lambda_k - \frac{1}{3} I_1 \lambda_k^{-1} \right) - p \lambda_k^{-1} I_3^{1/2}, \quad (4.14)$$

where  $\lambda_k$  are the principal specific elongations.

The complete system of equations that describe the mechanodiffusion processes of an individual liquid in cross-linked elastomers in the actual configuration includes transfer equations (4.4), the equilibrium equation (2.24) and the constitutive relations for the diffusion flux (4.1)–(4.3), the chemical potential (4.11), the Cauchy–Green stress tensor (4.12), and the incompressibility condition of the mixture (4.7). In the reference configuration, this system is represented by equations and relations (2.34), (4.5)–(4.8), (4.11), and (4.13).

The description of real objects based on the free-energy potential (2.9) is not always adequate. The procedure described above allows one to use more realistic models of elastomers for the description of mechanodiffusion processes. For this, it suffices to represent the free-energy potential in the form (2.44) and then use formulas (2.45)–(2.49).

**5. Kinetics of Swelling of Elastomers in Physically Aggressive Liquids.** One possible application of the proposed theory is the description of the swelling kinetics of elastomers in physically aggressive liquids — organic solvents and plasticizers. Under these conditions, elastomers can adsorb significant amounts of liquids and increase in volume. In this case, the geometric and physical nonlinearities are manifested in full measure.

Below we consider two problems of the swelling of an infinite flat layer of an elastomer in a powerful solvent. In the first problem, it is assumed that the elastomer layer is free and is not subjected to external mechanical actions. In the second problem, the elastomer is fixed to a rigid substrate. The first problem is of interest as a theoretical basis for experimental studies of the diffusion properties of elastomers using the sorption method [11], and the second is of interest as a model for the mechanodiffusion processes that occur in polymer coatings in contact with physically aggressive media [2].

We assume that, at the initial time, the elastomer does not contain a liquid and is undistorted. This state is chosen as the reference configuration, and the Cartesian coordinates related to the polymer matrix in this state are chosen as the body coordinates. The  $x$  axis is directed across the layer, and the remaining axes are directed along the layer. By virtue of the symmetry of both problems, we shall assume that all quantities that characterize the state of the elastomer depend only on the transverse  $x$  coordinate. The problems are considered in a one-dimensional formulation.

In the first case, we shall place the coordinate origin at the center of the layer, and the motion of the polymer matrix is sought in the form

$$X = X(x, t), \quad Y = \nu(t) y, \quad Z = \nu(t) z, \quad (5.1)$$

where  $(x, y, z)$  are the body coordinates, and  $(X, Y, Z)$  are coordinates that determine the actual configuration of the polymer matrix. Then, the principal specific elongations of the polymer matrix are as follows:

$$\lambda_x = \lambda = \frac{\partial X}{\partial x}, \quad \lambda_y = \lambda_z = \frac{\partial Y}{\partial y} = \frac{\partial Z}{\partial z} = \nu(t). \quad (5.2)$$

Hence, we have

$$J = I_3^{1/2} = \lambda \nu^2. \quad (5.3)$$

The equations and boundary conditions that describe the free swelling of the flat layer are represented in the reference configuration as follows:

$$\frac{\partial n_1^0}{\partial t} = \frac{\partial}{\partial x} \left( K_x^0 \frac{\partial \mu}{\partial x} \right); \quad (5.4)$$

$$\frac{\partial \sigma_x^0}{\partial x} = 0; \quad (5.5)$$

$$n_1^0(x, 0) = 0, \quad X(X, 0) = x \quad (0 < x < h); \quad (5.6)$$

$$\frac{\partial \mu(0, t)}{\partial x} = 0, \quad X(0, t) = 0; \quad (5.7)$$

$$\mu(h, t) = 0, \quad \sigma_x^0(h, t) = 0; \quad (5.8)$$

$$\int_0^h \sigma_y^0 dx = \int_0^h \sigma_z^0 dx = 0. \quad (5.9)$$

Here (5.6) are the initial conditions, (5.7) are conditions that imply the absence of diffusion flux and displacements of the polymer matrix along the  $x$  axis at the center of the layer, which follows from the symmetry of the process, (5.8) are conditions that imply the absence of thermodynamic equilibrium on the elastomer-liquid boundary and the absence of mechanical loading on the elastomer in the transverse direction, (5.9) is the condition of absence of external loading on the layer in the longitudinal direction, and  $2h$  is the initial thickness of the layer.

To these equations, we must add the condition of incompressibility of the mixture. Taking into account (4.7) and (4.8) and the initial condition, we have

$$J = \varphi_2^{-1}. \quad (5.10)$$

Hence it follows that the polymer and liquid concentrations are uniquely related to the volume strains of the polymer matrix:

$$\varphi_1 = 1 - J^{-1}, \quad n_1 = V_1^{-1}(1 - j^{-1}), \quad n_2 = V_2^{-1}J^{-1}.$$

In the reference configuration according to (2.35), we have

$$\varphi_1^0 = (J - 1), \quad n_1^0 = V_1^{-1}(J - 1), \quad n_2^0 = J^{-1}. \quad (5.11)$$

From (5.5) and (5.8) it follows that  $\sigma_x^0 = 0$ . Using this equation, we obtain an expression for the pressure and exclude it from all formulas. Reverting to (4.14), after rearrangements we find that  $p = C(\lambda^2 - I_1/3)/J$ . Substituting this relation into (4.11) and (4.14) and taking into account (5.3) and (5.10), we write the longitudinal stresses and the chemical potential as

$$\sigma_y^0 = \sigma_z^0 = C(\nu - \lambda^2/\nu); \quad (5.12)$$

$$\mu = RT[\ln \varphi_1 + (1 - BZ^{-1})\varphi_2 + \chi\varphi_2^2 + AZ^{-1}\varphi_2^{-1}\nu^{-4}]. \quad (5.13)$$

Substituting (5.12) into (5.9) and using (5.3), for the longitudinal elongation of the layer we have

$$\nu = \left( h^{-1} \int_0^h j^2(x, t) dx \right)^{1/6}. \quad (5.14)$$

The chemical potential, as follows from (5.13), is a function of two variables: the liquid concentration and the specific longitudinal elongation of the layer, which does not depend on the spatial coordinate. Hence, we can write the diffusion flux in Fick form

$$j_z^0 = -D(n_1^0, \nu) \frac{\partial n_1^0}{\partial x}, \quad (5.15)$$

where the diffusion coefficient  $D$  is a function of two variables:

$$D = K_x^0 \frac{\partial \mu}{\partial n_1^0}. \quad (5.16)$$

In the present work, we do not consider the effect of the concentration and diffusion dependences of the diffusion coefficient on the swelling kinetics of the elastomer. In what follows, we therefore assume that

$D = \text{const}$  and concentrate on the time dependence of the limiting concentration of the diffusant, which does not have analogs in the description of diffusion in undeformable materials.

We examine the case of large degrees of swelling for weakly cross-linked elastomers ( $Z \gg 1$ ). Assuming that  $\varphi_2 \ll 1$ , in the expression of the chemical potential (5.13), we expand  $\ln \varphi_1$  in powers of  $\varphi_2$  to the second order inclusive. Substituting the resulting series into the first equation of (5.8) and restricting ourselves to the basic terms of the series, we express the limiting degree of swelling of the elastomer in terms of the longitudinal elongation of the layer:

$$J(h, t) = \varepsilon^{-5/9} \nu^{4/3}.$$

Here  $\varepsilon = [AZ^{-1}(0.5 - \chi)^{-1}]^{3/5}$  is the volume fraction of the elastomer in the limiting swelling state (in the same approximation). Substituting here relation (5.14), we obtain

$$J(h, t) = \varepsilon^{-5/9} \left( h^{-1} \int_0^h J^2(x, t) dx \right)^{2/9}. \quad (5.17)$$

This boundary condition is nonlocal, because, on the right, it contains a linear functional that is defined on a set of functions that describe the distribution of the diffusant in the elastomer.

The final formulation of the problem is written as

$$u_t = u_{xx}; \quad (5.18)$$

$$u(x, 0) = 0, \quad u_x(0, t) = 0; \quad (5.19)$$

$$(1 - \varepsilon)u(1, t) + \varepsilon = \left( \int_0^1 [(1 - \varepsilon)u(x, t) + \varepsilon]^2 dx \right)^{2/9}. \quad (5.20)$$

Here we transform to dimensionless variables. The units of measurement for distance and time are the quantities  $h$  and  $h^2/D$ , respectively. The function  $u(x, t)$  takes values in the interval  $(0, 1)$  and is the dimensionless concentration of the diffusing liquid. It is related to the remaining quantities by the relations

$$n_1^0 = V_1^{-1}(\varepsilon^{-1} - 1)u(x, t), \quad J(x, t) = \varepsilon^{-1}[(1 - \varepsilon)u(x, t) + \varepsilon].$$

Thus, the problem of the swelling of the free plane elastomer layer is reduced to the boundary-value problem (5.18)–(5.20), whose solution allows one to completely describe the mechanodiffusion process, i.e., to determine the current distributions of stresses, strains, and the diffusant concentration in the layer in both the reference and actual configurations.

We study the behavior of the solution of the boundary-value problem (5.18)–(5.20) using approximate estimates. We consider two stages of the swelling process: initial and final. The initial stage is characterized by an insignificant effect of the inner boundary on the course of the process. Therefore, at sufficiently small times, diffusion into the layer of finite thickness can be treated as diffusion into a semiinfinite body. The solution of Eq. (5.18) is of the form

$$u(x, t) = ct^m \theta(\eta), \quad (5.21)$$

where the self-similar variable is  $\eta = (1 - x)/\sqrt{t}$  and the function  $\theta$  satisfies the conditions  $\theta(0) = 1$  and  $\theta(+\infty) = 0$ . Substituting (5.21) into (5.18) yields the following equation for the function  $\theta(\eta)$ :

$$\theta'' + \theta' \eta / 2 - m\theta = 0.$$

Solution (5.21) satisfies condition (5.20) only for  $\varepsilon = 0$ . In this case, we have  $m = 1/5$  and  $c = \left( \int_0^\infty \theta^2(\eta) d\eta \right)^{2m}$ , as can be verified by direct substitution. This solution can be regarded as an approximation of the exact solution. Obviously, the accuracy of this approximation is determined by the parameter  $\varepsilon$ .

Thus, the initial stage of the swelling process is approximately described by the function

$$u(x, t) = ct^0 \theta((1 - x)/\sqrt{t}). \quad (5.22)$$

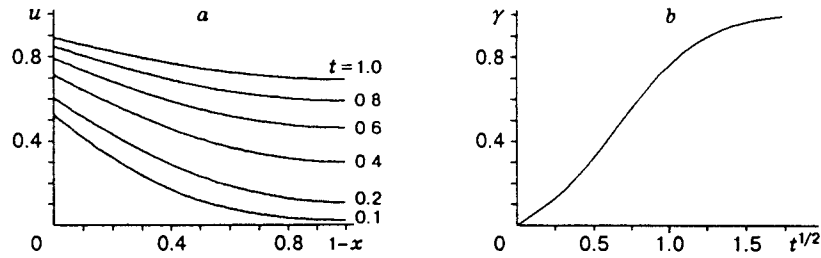


Fig. 1. Numerical results for the problem of swelling of a free flat elastomer layer ( $\varepsilon = 0.1$ ): (a) liquid distributions at various times; (b) kinetic curve of the swelling of the layer

To describe the final stage of swelling, we introduce the new variable  $v = 1 - u$  and linearize problem (5.18)–(5.20) with respect to this variable. Then, we have

$$v_t = v_{xx}, \quad v(x, 0) = 1, \quad v_x(0, t) = 0, \quad v(1, t) = \frac{4}{9} \int_0^1 v(x, t) dx.$$

Using the method of separation of variables, we obtain a solution in the form

$$v(x, t) = \sum_{k=1}^{\infty} a_k \exp(-\xi_k^2 t) \cos(\xi_k x), \quad (5.23)$$

where the values of  $a_k$  are determined from the initial conditions and the eigenvalues  $\xi_k$  are determined from the equation

$$\xi_k = (4/9) \tan \xi_k. \quad (5.24)$$

In sorption experiments, the swelling kinetics is described by the function

$$\gamma(t) = \int_0^1 u(x, t) dx, \quad (5.25)$$

which has the meaning of the amount of the liquid that is absorbed by the specimen for the time  $t$  normalized to unity [11]. Using the approximate solutions obtained, it is possible to establish the behavior of the kinetic curve for the free swelling of a flat extended specimen of an elastomer. Substituting (5.22) into (5.25) and taking into account the above reasoning for the initial stage of swelling, we have

$$\gamma(t) \simeq t^{0.7}. \quad (5.26)$$

Restricting ourselves to the first term of series (5.23), for the final stage we have

$$1 - \gamma(t) \simeq \exp(-\xi_1^2 t). \quad (5.27)$$

Figure 1 gives the results of numerical investigation of problem (5.18)–(5.20).

The swelling kinetics, described by formulas (5.26) and (5.27), differs markedly from the so-called kinetics of the normal type, which is traditionally used for the description of the sorption and diffusion of liquids and gases in polymers [11, 12]. The description of the normal sorption kinetics is based on the Fick diffusion model and on the assumption that the limiting diffusant concentration is constant. A characteristic feature of normal sorption is that, in the initial stage,  $\gamma(t) \simeq t^{1/2}$ , and the final stage is described by formula (5.27) with  $\xi_1 = \pi/2$ . All departures from such behavior, which are often observed in sorption experiments, are called anomalies. Rogers [12] gives a classification of anomalies of the sorption kinetics in polymers. According to this classification, the sorption kinetics described by formulas (5.26) and (5.27) is classified as the pseudonormal type.

We turn to the problem of the swelling of an elastomer layer fixed to a rigid substrate. The coordinate origin is placed on the elastomer–substrate boundary. The motion of the layer is given by formulas (5.2), in

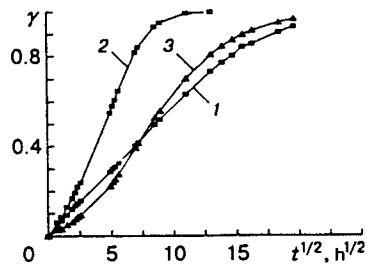


Fig. 2

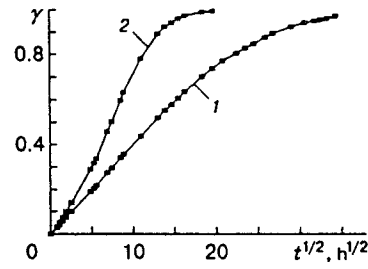


Fig. 3

Fig. 2. Swelling kinetics of PBU-1 ( $\epsilon = 0.345$ ) and PBU-2 elastomers ( $\epsilon = 0.127$ ) in dibutylsebacate: 1) fixed PBU-1 specimen; 2) free PBU-1 specimen; 3) free PBU-2 specimen.

Fig. 3. Swelling kinetics of PBU-1 in dibutylsebacate ( $\epsilon = 0.462$ ): 1) fixed specimen; 2) free specimen.

which we set

$$\nu = 1. \quad (5.28)$$

This means the absence of longitudinal deformations of the layer. Hence it follows that all state parameters of the layer are uniquely determined by its transverse strain. Equations and boundary conditions that describe the swelling of the fixed layer are identical to (5.4)–(5.8), except for condition (5.9), which is replaced by (5.28). From the same reasoning as for the first problem, we obtain expressions for the longitudinal stresses and the chemical potential. They are obtained in explicit form from (5.12) and (5.13) if we set  $\nu = 1$ . The chemical potential is a function of a single variable — the diffusant concentration. The first of relations (5.8) defines the following boundary concentration, which, in this case, is a constant. As a result, we come to the boundary-value problem that describes the swelling kinetics of the fixed layer:

$$u_t = u_{xx}, \quad u(x, 0) = 0, \quad u_x(0, t) = 0, \quad u(1, t) = 1. \quad (5.29)$$

Here the dimensionless variables have the same meaning as in the first problem. The initial thickness of the layer is  $h$ . The dimensionless concentration is defined so that the value  $u = 1$  corresponds to the liquid concentration in the equilibrium-swollen fixed layer.

The boundary-value problem (5.29) describes the sorption kinetics of the normal type [11, 12]. Thus, the type of swelling kinetics of an elastomer depends greatly on the external-loading conditions, as confirmed by direct experiments. Figures 2 and 3 show the results of experiments on swelling of fixed and free specimens of PBU-1 and PBU-2 elastomers, which are cross-linked polybutadiene urethane obtained by solidification of commercial SKU-DF-2 prepolymer solidified by a mixture of trimethylolpropane with 1,4-butanediol (PBU-1 elastomer) and a mixture of oligobutadienediol (molecular mass 2000) with trimethylolpropane (PBU-2 elastomer). The procedure for obtaining the elastomers is given in [13].

Specimens of the elastomers were fabricated in the form of disks 60 mm in diameter and 2 mm thick. Part of the PBU-1 specimens were glued on metal plates. The experiments on swelling were performed in two liquids: dibutylsebacate (DBS) and dioctylsebacate. The *S*-shaped kinetic swelling curves for free specimens in the coordinates  $(t^{1/2}, \gamma)$  indicate the anomalous type of sorption. This anomaly is most pronounced for the extremely swollen PBU-2–DBC system. In contrast to this, for the initial stage of swelling of fixed specimens, the kinetic curves have a distinct linear portion, which is an indication of normal absorption.

Thus, the general system of equations and constitutive relations of the nonlinear theory of mechanodiffusion for hyperelastic isotropic materials is formulated. These equations are derived as a result of a diffusion approximation from the dynamic theory of mixtures [3–5], which is extended in the present paper to the multicomponent case. The derivation is performed within the framework of rational thermomechanics,

based on the Clausius–Duhem inequality as the second law of thermodynamics. An advantage of this approach in this case is the possibility of establishing the general structure of equations and constitutive relations of the theory using the basic principles of thermomechanics and a minimum number of explicitly formulated assumptions. Unlike the approach of [3–5], the present theory is constructed in terms of the global stress tensor and chemical potentials. This is more natural in the description of molecular solutions from a thermodynamical viewpoint. The equations are written in invariant form with respect to the choice of the reference configuration. Owing to this, they become physically illustrative and allow one to formulate relatively easily constitutive relations for particular materials, pose boundary-value problems, and interpret experimental results by borrowing appropriate expedients and methods from the nonlinear theory of elasticity and mass-transfer theory.

The use of the nonlinear theory of mechanodiffusion for the description of the swelling of elastomers in organic solvents and plasticizers makes it possible to explain in a natural manner the cause and mechanism of the non-Fick behavior of kinetic sorption curves. The so-called anomalies of the sorption kinetics in extremely swollen materials are typical of such systems and are manifestations of the nonlinear character of the diffusion saturation and deformation of the material under extreme swelling conditions.

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