6

SWELLING

6.1 MODERN VIEWS ON KINETICS OF SWELLING OF CROSSLINKED ELASTOMERS IN SOLVENTS

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6.1.1 INTRODUCTION

Diffusion phenomena encountered in mass-transfer of low-molecular liquids play an important role in many technological processes of polymer manufacture, processing, and use of polymeric materials. Diffusion of organic solvents in crosslinked elastomers may cause considerable material swelling. In this case, the polymeric matrix experiences strains as large as several hundred percent, while a non-homogeneous distribution of a liquid due to diffusion results in establishing stress-strain state capable of affecting the diffusion kinetics. The processes of material deformation and liquid diffusion in such systems are interrelated and nonlinear in nature and are strongly dependent on physical and geometrical nonlinearities. Therefore, exact relations of nonlinear mechanics of elastic-deformable continuum are the mainstream of a sequential theory of mass-transfer processes of low-molecular liquids in elastomers.

The general principles of the development of nonlinear models of mass transfer in elastically deformed materials were developed in studies.[1,2] The general formulation of constitutive equations and the use of non-traditional thermodynamic parameters such as partial stress tensors and diffusion forces lead to significant difficulties in attempts to apply the theory to the description of specific objects.[3,4] Probably, because of this, the theory is little used for the solution of applied problems.

In the paper,[5] a theory for mechanical and diffusional processes in hyperelastic materials was formulated in terms of the global stress tensor and chemical potentials. The approach described in[1,2] was used as the basic principle and was generalized to the case of a multi-component mixture. An important feature of the work[5] is that, owing to the structure of constitutive equations, the general model can be used without difficulty to describe specific systems.

In the paper[6] the nonlinear theory[5] was applied to steady swelling processes of crosslinked elastomers in solvents. The analytical and numerical treatment reveals three

possible mechano-diffusion modes which differ qualitatively. Self-similar solutions obtained for these modes describe asymptotic properties at the initial stage of swelling. These modes are related to thermodynamical material properties. The theoretical predictions have been verified in the experiments on real elastomers.

6.1.2 FORMULATION OF SWELLING FOR A PLANE ELASTOMER LAYER

Consider an infinite plane elastomer layer of thickness 2h embedded in a low-molecular liquid. Suppose that the elastomer initially does not contain liquid and is unstrained. This state is taken as a reference configuration. Let us introduce the Cartesian coordinates (x,y,z) with the origin placed in the layer center and relate them to a polymer matrix. In the examined problem, the Cartesian coordinates will be used as the material coordinates. With reference to the layer, the x axis has a transverse direction and the other axes have longitudinal directions. In our approach, we define the problem under consideration as a one-dimensional problem, in which all quantities characterizing the elastomer state depend only on the x-coordinate.

On swelling, the layer experiences transversal and longitudinal deformations which can be written as

$$X = X(x,t) \quad Y = \nu(t)y \quad Z = \nu(t)z \qquad [6.1.1]$$

where (X,Y,Z) are the spatial Cartesian coordinates specifying the actual configuration of the polymeric matrix. From this it follows that the relative longitudinal stretch of the layer is $\lambda_2 = \lambda_3 = \nu(t)$ and the relative transversal stretch is $\lambda_1 = \lambda(x,t) = \partial X / \partial x$. The quantity

$$J = \lambda_1\lambda_2\lambda_3 = \lambda\nu^2 \qquad [6.1.2]$$

characterizes a local relative change in the material volume due to liquid absorption.

The boundary conditions and the relations describing free swelling of the plane layer in the reference configuration are represented in[5] as

$$\frac{\partial N_1}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial N_1}{\partial x}\right), \quad N_1 = N_1(x,t) \qquad [6.1.3]$$

$$\partial N_2 / \partial t = 0 \qquad [6.1.4]$$

$$\partial\sigma_1 / \partial x = 0 \qquad [6.1.5]$$

$$N_1(x,0) = 0 \qquad [6.1.6]$$

$$\partial N_1(0,t) / \partial x = 0, \quad X(0,t) = 0 \qquad [6.1.7]$$

$$\mu(h,t) = 0, \quad \sigma_1(h,t) = 0 \qquad [6.1.8]$$

$$\langle\sigma_2(x,t)\rangle = \langle\sigma_3(x,t)\rangle = 0 \qquad [6.1.9]$$

where:

N_1, N_2	the molar concentrations of the liquid and the chains of polymeric network of elastomer, respectively,
μ	the chemical potential of the liquid dissolved in material
σ_k	(k = 1,2,3) are the principal values of the Piola stress tensors.

The angular brackets denote integration with respect to coordinate x:

$$\langle \ldots \rangle = h^{-1} \int_0^h \ldots dx$$

Owing to the symmetry of the swelling process in the layer, the problem is solved for 0<x< h.

The equation of the liquid transport [6.1.3] in a plane layer has the form of a general diffusion equation except for the diffusion coefficient of the liquid, which, in the general case, is defined by the function $D = D(N_1,\nu)$, implying that it depends on the liquid concentration and the relative longitudinal stretch of the layer.[5] Eq. [6.1.4] is the law of conservation of matter for the polymeric matrix, and Eq. [6.1.5] states that the process of elastomer swelling is in the state of mechanical equilibrium. The initial condition is explicitly defined by Eq. [6.1.6]. The constraint that the diffusion flux and the displacements of polymeric matrix along x-axis in the layer center are absent is given by Eq. [6.1.7]. Eq. [6.1.8] has the physical meaning that there exists a thermodynamical equilibrium at the elastomer-liquid interface and that elastomer is not subjected to transverse mechanical loading, while Eq. [6.1.9] means that the layer does not experience longitudinal stretch under the external force.

The assumption that the elastomer and the liquid are incompressible media can be mathematically represented by an incompressibility condition, which in the present case is written as[5]

$$J = \phi^{-1} \qquad [6.1.10]$$

where the volume fraction of the polymer is

$$\phi = N_2 V_2 \,/\, (N_1 V_1 + N_2 V_2) \qquad [6.1.11]$$

where:

V_1 and V_2 the molar volumes of liquid and chains of the elastomer network, respectively

To make the definition of the examined problem complete, we need to add to the above model equations, the constitutive relations for mechanical stress tensor and chemical potential of a liquid. According to[5, 6] these equation are given by

$$\sigma_k = RTV_2^{-1}\left(\lambda_k - I_1\lambda_k^{-1} / 3\right) - pJ\lambda_k^{-1} \qquad [6.1.12]$$

$$\mu = \mu_{mix}(\phi) + RTZ^{-1}\phi^{1/3}\Gamma_1 / 3 + V_1 p \qquad [6.1.13]$$

$$\mu_{mix} = RT\left[\ln(1-\phi) + \phi + \chi\phi^2\right] \qquad [6.1.14]$$

where:

R	the gas constant per mole
T	the absolute temperature
μ_{mix}	the chemical potential of mixing
p	pressure
χ	the Flory-Huggins interaction parameter

$Z = V_2/V_1$
$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$
$\Gamma_1 = I_1/J^{2/3}$

The above equations follow from the classical high elasticity theory and the Flory theory of polymeric networks.[7]

From Eq. [6.1.5] and the second condition of Eq. [6.1.8], we find that $\sigma_1(x,t) = 0$. This equation together with Eq. [6.1.12] yields the expression for pressure. By substituting it in the formulas for chemical potential [6.1.13] and longitudinal stresses, we find, using Eqs. [6.1.2] and [6.1.10], that

$$\sigma_2 = \sigma_3 = RTV_2^{-1}\left(\nu - J^2/\nu^5\right) \qquad [6.1.15]$$

$$\mu = \mu_{mix}(1/J) + RTZ^{-1}J/\nu^4 \qquad [6.1.16]$$

A substitution of Eq. [6.1.15] in Eq. [6.1.9] gives an expression for longitudinal stretch of the layer

$$\nu^6 = \left\langle J^2(x,t)\right\rangle \qquad [6.1.17]$$

With consideration of Eq. [6.1.16], the boundary condition at x = h is transformed to

$$\mu_{mix}(1/J)RT + Z^{-1}J/\nu^4 = 0 \qquad [6.1.18]$$

Thus, the initial swelling problem for a plane layer is reduced to a boundary value problem for diffusion equation [6.1.3] with boundary conditions of Eqs. [6.1.6], [6.1.7], [6.1.17] and [6.1.18]. The solution to this problem provides a full description of swelling processes in the plane layer. In other words, using Eqs. [6.1.1], [6.1.2], [6.1.10] and [6.1.15] we can define a current distribution of a liquid through the layer and calculate the stress-strain state of the material.

It should be noted that boundary conditions of Eq. [6.1.18] and Eq. [6.1.17] specify the existence of positive feedback in the system, which is responsible for the onset of unsteady boundary regime during material swelling. The nonlinear distributed systems with positive feedback are generally known as active media and are distinguished for their complex and multimode response.[8] In free swelling, the response of elastomers is, in a sense, similar to that of active media. Such behavior is most pronounced when the extent of material swelling is high, which makes this case worthwhile for detailed investigation.

For high-swelling elastomers, the volume fraction of polymer in equilibrium swelling state denoted in the following as ε and the volume fraction of polymer at the elastomer-liquid interface $\phi = 1/J$ entering Eq. [6.1.18] are small quantities. The asymptotic behavior of the function $\mu_{mix}(\phi)$ at $\varphi \to 0$ is described by

$$\mu_{mix}(\phi)/RT = -b\phi^{\alpha} \qquad [6.1.19]$$

The constants b and α can be calculated using the Flory equation [6.1.14]. A second order expansion of $\ln(1-\phi)$ as a power series of ϕ gives $b = 1/2-\chi$ and $\alpha = 2$. The scaling approach gives a slightly different value of α, which is found to be $\alpha = 9/4$ (des Cloizeaux law[9]).

A volume fraction of the polymer in equilibrium swelling state can be determined by substituting Eq. [6.1.19] in Eq. 6.1.18] and setting $\phi = J^{-1} = \varepsilon$ and $\nu = \varepsilon^{-1/3}$, yields $\varepsilon \approx (bZ)^{-3/(3\alpha-1)}$. Then, using Eqs. [6.1.18], [6.1.19] and the last relation, we arrive at the following expression for the volumetric swelling ratio of the layer at the elastomer-liquid interface:

$$J \approx \varepsilon^{-1}\left(\varepsilon^{1/3}\nu\right)^{6d} \qquad [6.1.20]$$

where

$$d = \frac{2}{3(\alpha+1)} \qquad [6.1.21]$$

Note that approximate Eq. 6.1.20] defines the strain dependence of the equilibrium swell ratio of the elastomer in a liquid medium under conditions of biaxial symmetric material extension.

Substituting Eq. [6.1.17] in Eq. [6.1.20], we express the boundary swell ratio in terms of liquid distribution in the layer

$$J(h,t) = \varepsilon^{2d-1}\left\langle J^2(x,t)\right\rangle^d \qquad [6.1.22]$$

Then the problem is finally defined as

$$u_t = \left(k(u,l)u_x\right)_x; \quad x \in (0,1), \quad t > 0 \qquad [6.1.23]$$

$$u(x,0) = 0, \quad u_x(1,t) = 0 \qquad [6.1.24]$$

$$(1-\varepsilon)u(0,t) + \varepsilon = \left\langle\left[(1-\varepsilon)u(x,t) + \varepsilon\right]^2\right\rangle^d \qquad [6.1.25]$$

Here we assign dimensions to the variables. The quantities h and h^2/D_0 (where D_0 is the value of diffusion coefficient in the state of ultimate elastomer swelling) are used as the units of distance and time. For the sake of convenience we transform, the coordinate to $x \rightarrow 1\text{-}x$. Integrating for x between the limits from 0 to 1 in Eq. [6.1.25] is designated by angular brackets. The function u(x,t) takes the value over the interval (0,1) and represents a dimensionless concentration of penetrating liquid. It is related to the liquid concentration and local material swelling by the following equations:

$$N_1 = V_1\left(\varepsilon^{-1} - 1\right)u(x,t), \quad J(x,t) = \varepsilon^{-1}\left[(1-\varepsilon)u(x,t) + \varepsilon\right] \qquad [6.1.26]$$

The quantity $l = \varepsilon^{1/3}\nu$ represents the longitudinal layer stretch normalized to unity. By virtue of [6.1.17] and [6.1.26] we may write

$$l^6(t) = \left\langle\left[(1-\varepsilon)u(x,t) + \varepsilon\right]^2\right\rangle \qquad [6.1.27]$$

Dimensionless diffusion coefficient is defined by the formula k(u,l) = D(u,l)/D_0.

The longitudinal stresses in the layer (15) are expressed in terms of dimensionless stresses q(x,t) by

$$\sigma_2 = \sigma_3 = RTV_2^{-1} q(x,t) \qquad [6.1.28]$$

where according to Eqs. [6.1.15] and [6.1.27]

$$q(x,t) = \varepsilon^{-1/3} l(t) \left\{ 1 - \left[(1-\varepsilon) u(x,t) + \varepsilon \right]^2 / l^6(t) \right\} \qquad [6.1.29]$$

Consider two functions

$$g_1(t) = \langle u(x,t) \rangle, \quad g_2(t) = \langle u^2(x,t) \rangle \qquad [6.1.30]$$

which are integral characteristics of swelling kinetics for a plane layer and can be determined from experiments. The first function characterizes a relative amount of liquid absorbed by a polymer in time t and the second function according to Eq. [6.1.27] is related to longitudinal layer deformation. For high-swelling elastomers

$$g_2(t) \approx l^6(t) \qquad [6.1.31]$$

The numerical results obtained by solving model problem of Eqs. [6.1.23] - [6.1.25] for a constant diffusion coefficient are plotted in Figure 6.1.1.[6] The obtained curves show the evolution of penetrating liquid concentration and longitudinal stresses. It is seen that the boundary liquid concentration during swelling monotonically increases.

6.1.3 DIFFUSION KINETICS OF PLANE LAYER SWELLING

Consider two stages of swelling process in a plane layer - the initial and final. In the initial stage, the influence of the opposite layer boundary on the swelling process is inessential and therefore diffusion in a layer of finite thickness at sufficiently small values of time can be considered as the diffusion in half-space.

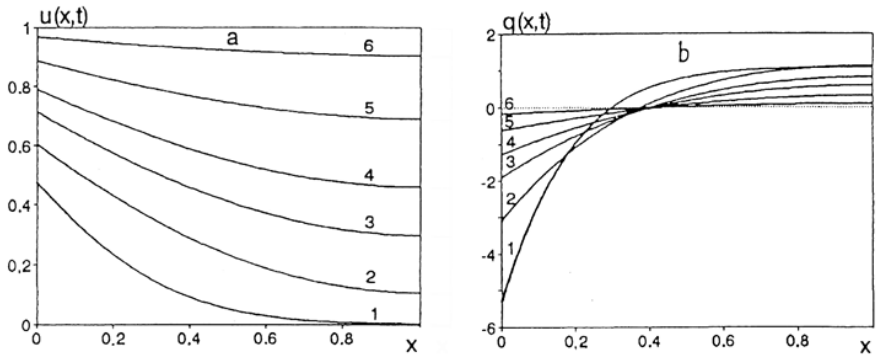

Figure 6.1.1. Distribution of penetrating liquid (a) and longitudinal stresses (b) during swelling of a plane layer with constant diffusion coefficient k(u,l) = 1 at ε = 0.1 and d = 2/9: 1 - t = 0.05; 2 - t = 0.2; 3 - t = 0.4; 4 - t = 0.6; 5 - t = 1; 6 - t = 1.8. [Adapted, by permission, from E. Ya. Denisyuk, V. V. Tereshatov, *Vysokomol. soed.*, **A42**, 74 (2000)].

At the very beginning of the swelling process the amount of absorbed liquid is rather small. Hence we may set u(x,t) ≈ 0 in the right-hand parts of Eqs. [6.1.25] and [6.1.27] which results in

$$u(0,t) \approx \psi_0 = \left(\varepsilon^{2d} - \varepsilon\right) / (1-\varepsilon), \quad l(t) \approx \varepsilon^{1/3}$$

and Eq. [6.1.23] becomes an usual parabolic equation describing diffusion on a half-line with constant boundary concentration ψ_0. It has self-similar solution of the form $u(x,t)=\psi_0\theta(x/t^{1/2})$. The function $\theta(\xi)$ satisfies the equation $(k(\theta,\varepsilon^{1/3})\theta')' + \xi\theta'/2 = 0$ and the boundary conditions

$$\theta(0) = 1, \quad \theta(+\infty) = 0 \qquad [6.1.32]$$

From this follows the expression for the integral process characteristics

$$g_1(t) = \psi_0 M_1 t^{1/2}, \quad g_2(t) = \psi_0^2 M_2 t^{1/2}$$

where

$$M_p = \int_0^\infty \theta^p(\xi)d\xi \quad p = 1,2 \qquad [6.1.33]$$

These relations define the asymptotic properties of swelling at $t \to 0$.

As more and more amount of the liquid is absorbed, the longitudinal strains in the layer increase. By virtue of Eq. [6.1.25], this causes the growth of liquid concentration at the boundary. For high-swelling materials at sufficiently large values of time, all terms in Eq. [6.1.25] involving ε as a multiplier factor can be neglected to the first approximation. The resulting expression is written as

$$u(0,t) = \left\langle u^2(x,t)\right\rangle^d \qquad [6.1.34]$$

where the angular brackets denote integrating for x in the limits from 0 to +∞.

Since for arbitrary dependence of k(u,l) a boundary-value solution of equation [6.1.23] on the half-line with boundary condition of Eq. [6.1.34] cannot be represented in a similar form, we restrict our consideration to a model problem with diffusion coefficients defined by

$$k(u,l) = u^s, \quad s \geq 0 \qquad [6.1.35]$$

$$k(u,l) = u^s l^{6p}, \quad s \geq 0, \quad p \geq 0 \qquad [6.1.36]$$

(Let us agree that s = 0 corresponds to a constant diffusion coefficient k(u,l) = 1). The analysis of this problem allows us to qualitatively explain many mechanisms of diffusion kinetics of elastomer swelling.

First, consider the diffusion coefficient defined by Eq. [6.1.35]. In this case, Eq. [6.1.23] on the half-line has a variety of self-similar solutions, which can be written as

$$u(x,t) = \psi(t)\theta\left(x / \varphi(t)\right) \qquad [6.1.37]$$

where the function $\theta(\xi)$ satisfies conditions of Eq. [6.1.32] and defines the profile of the diffusion wave, $\psi(t)$ describes boundary conditions and $\varphi(t)$ the function specifies the penetration depth of diffusion wave.

Eq. [6.1.37] satisfies the boundary condition of Eq. [6.1.34] and Eq. [6.1.23] on the half-line with the diffusion coefficient of Eq. [6.1.35] in the following cases: 1) $\psi(t)$, $\varphi(t)$ are the functions of power type (power swelling mode); 2) $\psi(t)$, $\varphi(t)$ are the function exponentially depending on time (exponential swelling mode); 3) $\psi(t) \sim (t_0 - t)^m$, $\varphi(t) \sim (t_0 - t)^n$, where m, n < 0 (blow-up swelling mode).

Power swelling mode occurs at sufficiently small values of s. In this case, the amount of absorbed liquid, boundary concentration, the depth of diffusion wave penetration and the longitudinal layer deformation are the power function of time. If the parameter s approaches the critical value

$$s_c = 2 / d - 4 \qquad [6.1.38]$$

Swelling process is governed by exponential law. And finally, if $s > s_c$, the swelling mode is of a blow-up nature. The solutions describing these modes are given below.

I. Power mode ($s < s_c$):

$$u(x,t) = M_2^{2m} t^m \theta(\xi), \quad \xi = x / M_2^{ms} t^n \qquad [6.1.39]$$

$$g_1(t) = M_1 M_2^{2q-1} t^q, \quad g_2(t) = M_2^{2r} t^r \qquad [6.1.40]$$

$$m = \frac{1}{s_c - s}, \quad n = \frac{1/d - 2}{s_c - s}, \quad q = \frac{1/d - 1}{s_c - s}, \quad r = \frac{1}{d(s_c - s)} \qquad [6.1.41]$$

II. Exponential mode ($s = s_c$):

$$u(x,t) = \exp\left\{M_2^2 (t - t_0)\right\}\theta(\xi), \; \xi = x M_2 / \exp\left\{s_c M_2^2 (t - t_0) / 2\right\}$$

$$g_1(t) = (M_1 / M_2)\exp\left\{(s_c / 2 + 1) M_2^2 (t - t_0)\right\}$$

$$g_2(t) = \exp\left\{(s_c / 2 + 1) M_2^2 (t - t_0)\right\}$$

III. Blow-up mode ($s > s_c$):

$$u(x,t) = M_2^{2m} (t_0 - t)^m \theta(\xi), \quad \xi = x / M_2^{ms} (t_0 - t)^n$$

$$g_1(t) = M_1 M_2^{2q-1} (t_0 - t)^q, \quad g_2(t) = M_2^{2r} (t_0 - t)^r$$

where the exponents are defined by Eqs. [6.1.41] but if $s > s_c$, then m, n, q, r<0.

For power and blow-up swelling modes $\theta(\xi)$ are derived from the equation $(\theta^s \theta')' + |n| \xi \theta' - |m| \theta = 0$. For an exponential mode, this equation will be valid if we put

$n=s_c/2$ and $m=1$. The constants M_1 and M_2 are evaluated from Eq. [6.1.33] and the constant t_0 can be estimated by the order of magnitude from the condition $u(0,t_0)\sim\psi_0\sim\varepsilon^{2d}$. For the exponential mode, we have $t_0 \sim -2dM_2^{-2} \ln(\varepsilon)$, and for the blow-up mode, $t_0 \sim M_2^{-2}\, \varepsilon^{2d/m}$.

It is worth noting that at $m = 1/s$, which holds only if $s = 1/d - 2$, solution of Eq. [6.1.39] is expressed in terms of primary functions and describes the diffusion wave propagating with a constant velocity d:

$$u(x,t) = (1 - 2d)^{1/s}\,(dt - x)^{1/s}$$

The solution describing the blow-up mode turns into infinity at the finite time. In the global sense the boundary-value problems admitting such solutions are time unsolvable and are generally applied to modeling high rate physical-chemical processes.[10] It is quite evident that all solutions to the swelling problem for a layer of finite thick are limited and each of the self-similar solutions presented in this study describes asymptotic properties of diffusion modes at initial well-developed stage of swelling.

At the final swelling stage $u(x,t) \to 1$. In this case, an approximate solution to the problem can be obtained by its linearization in the vicinity of equilibrium $u = 1$. To this end, one needs to introduce a variable $v(x,t) = 1 - u(x,t)$. After transformation we get

$$v_t = v_{xx}, \quad v_x(1,t) = 0, \quad v(0,t) = 2d\langle v(x,t)\rangle$$

By making use of the method of variable separation, we find

$$v(x,t) = \sum_{k=1}^{\infty} a_k \exp\left(-\alpha_k^2 t\right)\cos\left[\alpha_k (1-x)\right] \qquad [6.1.42]$$

where the values of α_k are determined from the equation

$$\alpha_k = 2d \tan(\alpha_k) \qquad [6.1.43]$$

Restricting ourselves to the first term of a series Eq. [6.1.42], we can write for the final swelling stage the equation of kinetic curve

$$g_1(t) = 1 - (a_1 / \alpha_1)\exp\left(-\alpha_1^2 t\right)\sin(\alpha_k) \qquad [6.1.44]$$

The above expressions allow us to describe the shape of kinetic curves $g_1(t)$ in general terms. In particular, as it follows from Eqs. [6.1.39] - [6.1.41] at $q < 1$, the kinetic curves in the coordinates (t,g_1) are upward convex and have the shape typical for pseudo-normal sorption. This takes place at $s<s_c/2-1$. If $s=s_c/2-1$, then $q = 1$, which corresponds to a linear mode of liquid absorption. At $s>s_c/2-1$ the lower part of the kinetic curve is convex in a downward direction and the whole curve becomes S-shaped. Note that in terms of coordinates $(t^{1/2},g_1)$ at $s \geq 0$ all the kinetic curves are S-shaped. Hence, the obtained solutions enable one to describe different anomalies of sorption kinetics observed in the experiments on elastomer swelling in low-molecular liquids.

Figure 6.1.2[6] gives the results of numerical solution to problems of Eq. [6.1.25] with diffusion coefficient defined by Eq. [6.1.35]. The kinetic curves of swelling at different values of s are depicted in Figure 6.1.3.[6]

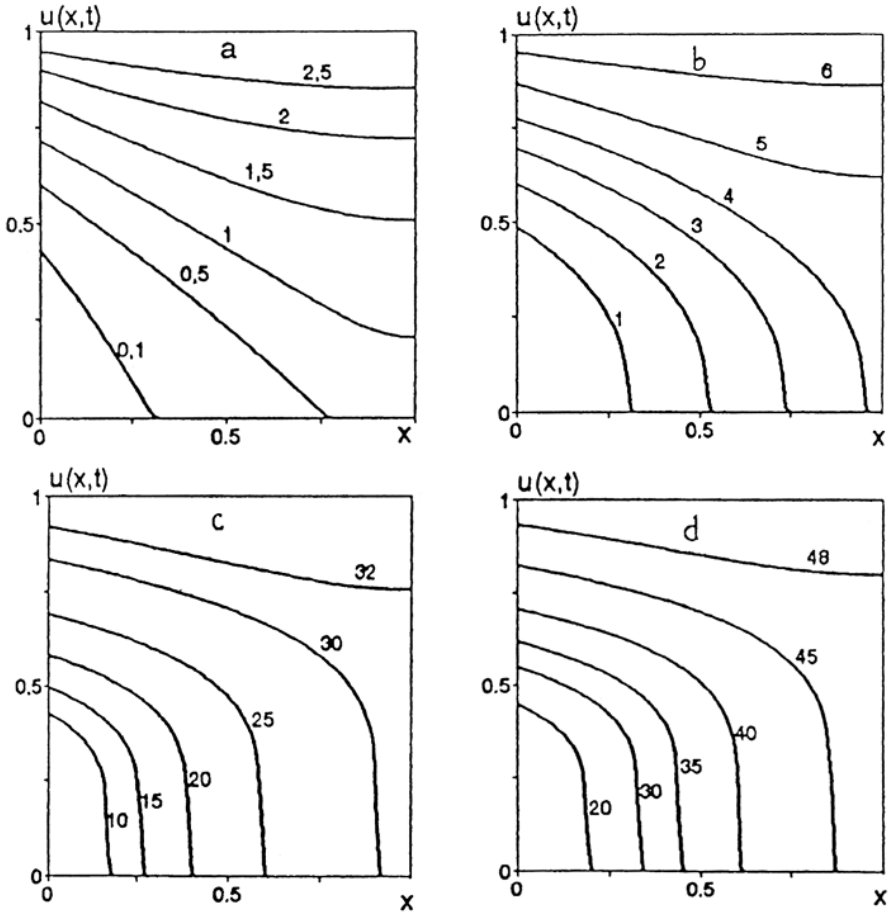

Figure 6.1.2. Diffusion kinetics of plane layer swelling for diffusion coefficient $k(u)=u^s$ at $\varepsilon = 0.1$ and $d = 2/9$; a, b are power swelling modes at $s = 1$ and $s = 2.5$, respectively; c - exponential swelling mode ($s=5$); d - blow-up swelling mode ($s = 5.5$). Numerals over curves denote correspond to instants of time. [Adapted, by permission, from E. Ya. Denisyuk, V. V. Tereshatov, *Vysokomol. soed.*, **A42**, 74 (2000)].

Here it is to be noted that strain dependence of the diffusion coefficient described by Eq. [6.1.36] does not initiate new diffusion modes. The obtained three self-similar solutions hold true. Only critical value s_c is variable and is defined by expression $s_c = (2-p)/d-4$. This fact can be supported by a direct check of the solutions.

6.1.4 EXPERIMENTAL STUDY OF ELASTOMER SWELLING KINETICS

The obtained solutions can be applied to experimental study of the diffusive and thermodynamic properties of elastomers. In particular, with the relation

$$s = 2/d - 4 - (1/d - 1)/q \qquad [6.1.45]$$

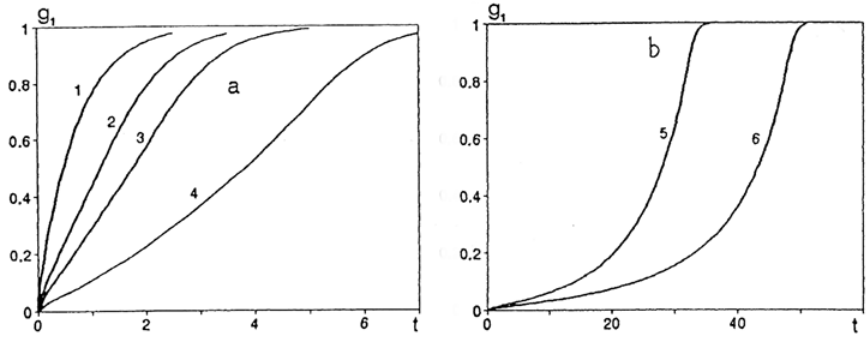

Figure 6.1.3. Kinetic curves of plane layer swelling at different values of concentration dependence of diffusion coefficient (ε = 0.1, d = 2/9): a - power law mode (1 - s = 0; 2 - s = 1; 3 - s = 1.5; 4 - s = 2.5); b - exponential (5 - s = 5) and blow-up mode (6 - s = 5.5). [Adapted, by permission, from E. Ya. Denisyuk, V. V. Tereshatov, *Vysokomol. soed*., **A42**, 74 (2000)].

following from Eqs. [6.1.38] and [6.1.41] we can estimate the concentration dependence of the diffusion coefficient of a liquid fraction in elastomer. According to Eq. [6.1.40] the parameter q is determined from the initial section of the kinetic swelling curve.

Experimental estimates of the parameter r can be obtained from the strain curve l(t) using Eqs. [6.1.31] and [6.1.40]. Then by making use of the formula

$$d = 1 - q/r \qquad [6.1.46]$$

following from Eq. [6.1.41] we can evaluate the parameter d which characterizes the strain dependence of the equilibrium swelling ratio of elastomer under symmetric biaxial extension in Eq. [6.1.45]. Generally the estimation of this parameter in tests on equilibrium swelling of strained specimens proves to be a tedious experimental procedure.

The value of diffusion coefficient in an equilibrium swelling state can be determined from the final section of kinetic swelling curve using Eq. [6.1.44], which is expressed in terms of dimensional variables as

$$g_1(t) = 1 - C\exp(-\alpha_1^2 D_0 t / h^2) \qquad [6.1.47]$$

where α_1 is calculated from Eq. [6.1.43). For d = 2/9, $\alpha_1 \approx 1.2220$.

Note that all these relations are valid only for sufficiently high values of elastomer swelling ratio.

The obtained theoretical predictions have been verified in experiments on real elastomers. The elastomers tested in our experiments were amorphous polybutadiene urethanes (PBU) with polymer network of different density: 0.3 kmol/m^3 (PBU-1), 0.05 kmol/m^3 (PBU-2), 0.2 kmol/m^3 (PBU-3), 0.1 kmol/m^3 (PBU-4). Oligooxypropylene triol - Laprol 373 was used as a crosslinking agent at the curing of prepolymer of oligobutadiene diol. The elastomer specimens were manufactured in the form of disks, 35 mm in diameter and 2 mm thick. The kinetics of specimen swelling was determined in low-molecular liquids: toluene, dibutyl sebacate (DBS), dioctyl sebacate (DOS).

The typical kinetic and strain curves of free swelling are given in Figure 6.1.4.[6] The S-shape of the kinetic swelling curves in terms of coordinates ($t^{1/2}$, g_1) is indicative of

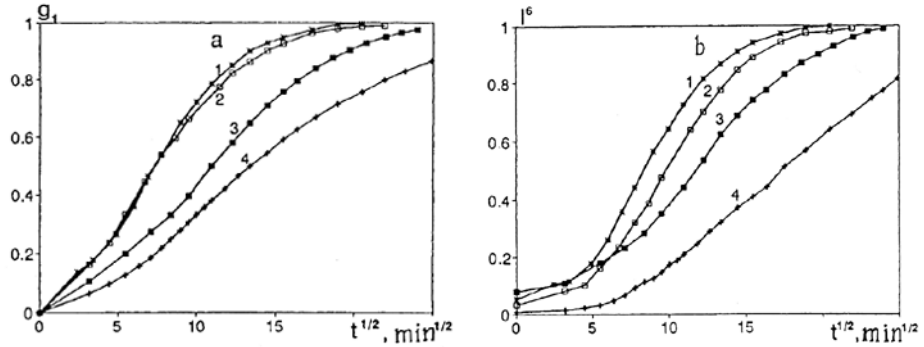

Figure 6.1.4. Kinetic (a) and strain (b) curves of elastomer swelling in toluene: 1 - PBU-3; 2 - PBU-4; 3 - PBU-1; 4 - PBU-2. [Adapted, by permission, from E. Ya. Denisyuk, V. V. Tereshatov, *Vysokomol. soed*., **A42**, 74 (2000)].

abnormal sorption. The values of parameters q and r were obtained from kinetic and strain curves using the regression method. The values of correlation coefficient were 0.997 - 0.999 and 0.994 - 0.998 respectively. The obtained data and Eqs. [6.1.45], [6.1.46] were then used to calculate s and d. The diffusion coefficients were defined by the kinetic curves in terms of Eq. [6.1.47] under the assumption that d = 2/9. The obtained results were summarized in Table 6.1.1.[6] The analysis of these data shows that swelling of the examined elastomers is of power-mode type. The concentration dependence of the liquid diffusion coefficient defined by the parameter s is found to be rather weak. For elastomers under consideration no exponential or blow-up swelling modes have been observed.

Table 6.1.1. Experimental characteristics of elastomer swelling kinetics[6]

Elastomer/Liquid	ε	q	r	s	d	D_0, cm^2/s
PBU-1/toluene	0.278	0.68	0.84	0	0.19	1.4×10^{-6}
PBU-2/toluene	0.093	0.83	1.09	0.8	0.24	4.9×10^{-7}
PBU-3/toluene	0.230	0.78	1.02	0.5	0.24	1.3×10^{-6}
PBU-4/toluene	0.179	0.71	0.97	0	0.27	1.4×10^{-6}
PBU-1/DBS	0.345	0.67	0.92	0	0.27	6.2×10^{-8}
PBU-2/DBS	0.128	0.78	1.04	0.5	0.25	2.5×10^{-8}
PBU-3/DBS	0.316	0.67	0.83	0	0.19	6.6×10^{-8}
PBU-4/DBS	0.267	0.69	0.88	0	0.21	7.4×10^{-8}
PBU-1/DOS	0.461	0.67	0.81	0	0.17	1.8×10^{-8}
PBU-4/DOS	0.318	0.63	0.81	0	0.22	3.4×10^{-8}

It is of interest to note that experimental values of the parameter d characterizing the strain dependence of equilibrium swelling ratio for elastomers subjected to uniform biaxial extension closely approximate the theoretical values. It will be recalled that this parameter is specified by Eq. [6.1.21]. Moreover, the Flory theory defines it as d = 2/9 = 0.22(2),

whereas the des Cloizeaux law provides $d \approx 0{,}205$, which suggests that the proposed model of elastomer swelling performs fairly well.

6.1.5 CONCLUSIONS

In this section, we have developed a geometrically and physically nonlinear model of swelling processes for an infinite plane elastomeric layer and obtained approximate solutions describing different stages of swelling at large deformations of a polymeric matrix. We have identified the strain-stress state of the material caused by diffusion processes and analyzed its influence on the swelling kinetics.

It has been found that a non-stationary boundary regime initiated by deformations arising in elastomer during swelling and increasing a thermodynamical compatibility of elastomer with a liquid is the main reason for swelling anomalies observed in the experiments. Anomalies of sorption kinetics turn out to be a typical phenomenon observable to one or another extent in elastic swelling materials.

The theory predicts the possibility for qualitatively different diffusion modes of free swelling. A particular mode is specified by a complex of mechanical, thermodynamical, and diffusion material properties. The results of analytical and numerical solutions for a plane elastomer layer show that the swelling process may be governed by three different laws resulting in the power, exponential, and blow-up swelling modes. Experimentally it has been determined that in the examined elastomers the swelling mode is governed by the power law. The existence of exponential and blow-up swelling modes in real materials is still an open question.

New methods have been proposed, which allow one to estimate the concentration dependence of liquid diffusion in elastomer and strain dependence of equilibrium swelling ratio under conditions of symmetric biaxial elastomer extension in terms of kinetic and strain curves of swelling.

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6.2 EQUILIBRIUM SWELLING IN BINARY SOLVENTS

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Depending on the purposes and operating conditions of polymer material processing, the opposite demands to solubility of low-molecular-mass liquids in polymers exist. The products of polymer materials designed for use in contact with solvents should be stable against relative adsorption of these liquids. On the contrary, the well dissolving polymer solvents are necessary to produce the polymer films. The indispensable condition of creation of the plasticized polymer systems (for example, rubbers) is the high thermodynamic compatibility of plasticizers with the polymer basis of material.

Hence, it immediately follows the statement of the problem of regulation of thermodynamic compatibility of polymers with low-molecular-mass liquids in a wide range of its concentration in polymer material. The problem of compatibility of crosslinked elastomers with mixed plasticizers and volatile solvents is thus of special interest.

Depending on ratios between solubility parameters of the solvent 1, δ_1, of the solvent 2, δ_2, and polymer, δ_3, solvents can be distinguished as "symmetric" liquids and "non-symmetric" ones. The non-symmetric liquids are defined as a mixture of two solvents of variable composition, solubility parameters δ_1 and δ_2 which are larger or smaller than solubility parameter of polymer ($\delta_2 > \delta_1 > \delta_3$, $\delta_3 > \delta_2 > \delta_1$). The symmetric liquid (SL) with relation to polymer is the mixture of two solvents, whose solubility parameter, δ_1, is smaller, and parameter, δ_2, is larger than the solubility parameter of polymer, δ_3.

The dependence of equilibrium swelling on the non-symmetric liquid composition does not have a maximum, as a rule.[1] Research on swelling of crosslinked elastomers in SL is particularly interested in the regulation of thermodynamic compatibility of network polymers and binary liquids. Swelling in such liquids is characterized by the presence of maximum on the curve of dependence of network polymer equilibrium swelling and composition of a liquid phase.[2,3] The extreme swelling of crosslinked polymers of different polarity in SL was discussed elsewhere.[3] The following elastomers were used as samples: a crosslinked elastomer of ethylene-propylene rubber SCEPT-40 [$\delta_3 = 16$ $(MJ/m^3)^{1/2}$, $(\nu_e/V_0)_x = 0.24$ kmol/m^3], crosslinked polyester urethane, PEU, from copolymer of propylene oxide and trimethylol propane [$\delta_3 = 18.3$ $(MJ/m^3)^{1/2}$, $(\nu_e/V_0)_x = 0.27$ kmol/m^3], crosslinked polybutadiene urethane, PBU, from oligobutadiene diol [$\delta_3 = 17.8$ $(MJ/m^3)^{1/2}$, $(\nu_e/V_0)_x = 0.07$ kmol/m^3] and crosslinked elastomer of butadiene-nitrile rubber [$\delta_3 = 19$ $(MJ/m^3)^{1/2}$, $(\nu_e/V_0)_x = 0.05$ kmol/m^3].

The samples of crosslinked elastomers were swollen to equilibrium at 25°C in 11 SLs containing solvents of different polarity. The following regularities were established. With decrease in the solubility parameter value of component 1 (see Table 6.2.1) in SL ($\delta_1 < \delta_3$), the maximum value of equilibrium swelling, Q, shifts to the field of larger concentration of component 2 in the mixture (Figures 6.2.1 and 6.2.2). On the contrary, with decrease in the

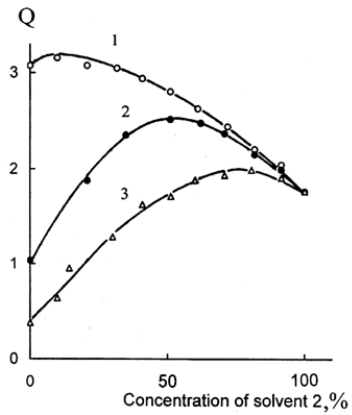

Figure 6.2.1. Dependence of equilibrium swelling of PEU on the acetone concentration in the mixtures: 1-toluene-acetone, 2-cyclohexane-acetone, 3-heptane-acetone. [Adapted, by permission, from V. V. Tereshatov, M. I. Balashova, A. I. Gemuev, **Prediction and regulating of properties of polymeric materials**, *Ural Branch of AS USSR Press*, Sverdlovsk, 1989, p. 3.]

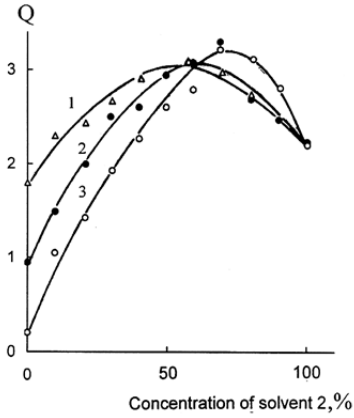

Figure 6.2.2. Dependence of equilibrium swelling of PBU on the DBP (component 2) concentration in the mixtures:1-DOS-DBP, 2-TO-DBP, 3- decane-DBP. [Adapted, by permission, from V. V. Tereshatov, M. I. Balashova, A. I. Gemuev, **Prediction and regulating of properties of polymeric materials**, *Ural Branch of AS USSR Press*, Sverdlovsk, 1989, p. 3.]

solubility parameter δ_2 (see Table 6.2.1) of components 2 ($\delta_2 > \delta_3$), the maximum Q corresponds to composition of the liquid phase enriched by component 1 (Figure 6.2.3).

Table 6.2.1. Characteristics of solvents and plasticizers at 298K. [Adapted, by permission, from V. V. Tereshatov, M. I. Balashova, A. I. Gemuev, Prediction and regulating of properties of polymeric materials, *Ural Branch of AS USSR Press*, Sverdlovsk, 1989, p. 3.]

Solvent/plasticizer	ρ, kg/m^3	V$\times 10^6$, m^3	δ, (MJ/m^3)$^{1/2}$
Cyclohexane	779	109	16.8
Heptane	684	147	15.2
Decane	730	194	15.8
Toluene	862	106	18.2
1,4-Dioxane	1034	86	20.5
Acetone	791	74	20.5
Ethyl acetate	901	98	18.6
Amyl acetate	938	148	17.3
Dibutyl phthalate	1045	266	19.0
Dioctyl sebacate	913	467	17.3
Transformer oil	890	296	16.0

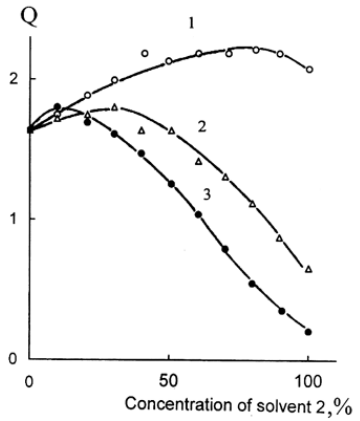

Figure 6.2.3. Dependence of equilibrium swelling of the crosslinked elastomer SCEPT-40 on the concentration of component 2 in the mixtures: 1-heptane-toluene, 2-heptane-amyl acetate, 3-heptane-ethyl acetate. [Adapted, by permission, from V. V. Tereshatov, M. I. Balashova, A. I. Gemuev, **Prediction and regulating of properties of polymeric materials**, *Ural Branch of AS USSR Press*, Sverdlovsk, 1989, p. 3.]

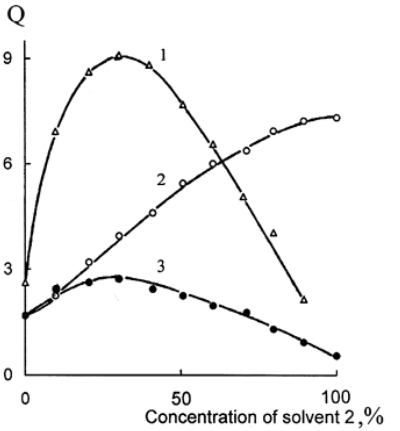

Figure 6.2.4. Dependence of equilibrium swelling of the crosslinked elastomer SCN-26 on the concentration of component 2 in the mixtures: 1-toluene-acetone, 2-ethyl acetate-dioxane, 3-ethyl acetate-acetone. [Adapted, by permission, from V. V. Tereshatov, M. I. Balashova, A. I. Gemuev, **Prediction and regulating of properties of polymeric materials**, *Ural Branch of AS USSR Press*, Sverdlovsk, 1989, p. 3.]

Neglecting the change of volume on mixing, the solubility parameter of the mixture of two liquids is represented by:

$$\delta_{12} = \delta_1 \varphi_1 + \delta_2 \varphi_2$$

where:

φ_1 and φ_2 volume fractions of components 1 and 2

More exact evaluation of the δ_{12} value is possible if the experimental data on enthalpy of mixing, ΔH, of components of SL are taken into account:[4]

$$\delta_{12} = \left(\delta_1^2 \varphi_1 + \delta_2^2 \varphi_2 - \Delta H / V_{12} \right)^{1/2}$$

With a change in δ_1 and δ_2 parameters, the SL composition has the maximum equilibrium swelling which corresponds to shifts in the field of composition of the liquid phase. The δ_{12} parameter is close or equal to the value of the solubility parameter of polymer. Such a simplified approach to the extreme swelling of polymers in liquid mixtures frequently works very well in practice. If there is a maximum on the curve of swelling in SL, then the swelling has an extreme character (11 cases out of 12) (Figures 6.2.1-6.2.4).

The parameter of interaction, χ_{123}, between polymer and a two-component liquid can be used as a co-solvency criterion for linear polymers (or criterion of extreme swelling), more general, than the equality ($\delta_{12} = \delta_3$):[5]

$$\chi_{123} = \chi_{13} \varphi_1 + \chi_{23} \varphi_2 - \varphi_1 \varphi_2 \chi_{12} \qquad [6.2.1]$$

where:

χ_{13} and χ_{23} parameters of interaction of components 1 and 2 with polymer, correspondingly
χ_{12} parameter of interaction of components 1and 2 of liquid mixture

In the equation obtained from the fundamental work by Scott,[5] mixed solvent is represented as "a uniform liquid" with the variable thermodynamic parameters depending on composition.

If the χ_{123} value is considered as a criterion of existence of a maximum of equilibrium swelling of polymer in the mixed solvent, a maximum of Q should correspond to the minimum of χ_{123}. For practical use of Eq. [6.2.2] it is necessary to know parameters χ_{13}, χ_{23}, and χ_{12}. The values χ_{13} and χ_{23} can be determined by the Flory-Rehner equation, with data on swelling of a crosslinked elastomer in individual solvents 1 and 2. The evaluation of the χ_{12} value can be carried out with use of results of the experimental evaluation of vapor pressure, viscosity and other characteristics of a binary mixture.[6,7]

To raise the forecasting efficiency of prediction force of such criterion as χ_{123} minimum, the amount of performance parameters determined experimentally must be reduced. For this purpose, the following expression for the quality criterion of the mixed solvent (the analogy with expression of the Flory-Huggins parameter for individual solvent-polymer system) is used:

$$\chi_{123} = \chi^s_{123} + \frac{V_{12}}{RT}(\delta_3 - \delta_{12})^2 \quad V_{12} = V_1 x_1 + V_2 x_2 \qquad [6.2.2]$$

where:

V_{12} molar volume of the liquid mixture
V_1, V_2 molar volumes of components 1 and 2
x_1, x_2 molar fractions of components 1 and 2 in the solvent
R universal gas constant
T temperature, K.
χ^s_{123} constant, equal to 0.34

The values of entropy components of parameters χ^s_{13} and χ^s_{23} (essential for quality prediction)[8] were taken into account. Using the real values of entropy components of interaction parameters χ^s_{13} and χ^s_{23}, we have:

$$\chi^s_{13} = \chi_{13} - \frac{V_1}{RT}(\delta_3 - \delta_1)^2 \qquad [6.2.3]$$

$$\chi^s_{23} = \chi_{23} - \frac{V_2}{RT}(\delta_3 - \delta_2)^2 \qquad [6.2.4]$$

quality criterion of mixed solvent is represented by:[3]

$$\chi_{123} = \chi^s_{13}\varphi_1 + \chi^s_{23}\varphi_2 + \frac{V_{12}}{RT}(\delta_3 - \delta_{12})^2 \qquad [6.2.5]$$

The values of parameters χ_{13} and χ_{23} were calculated from the Flory-Rehner equation, using data on swelling of crosslinked polymer in individual solvents, the values χ^s_{13}, χ^s_{23}, and χ_{123} were estimated from Eqs. [6.2.3-6.2.5). Then equilibrium swelling of elastomer in SL was calculated from the equation similar to Flory-Rehner equation, considering the mix-

ture as a uniform liquid with parameters χ_{123} and V_{12} variable in composition. The calculated ratios of components of mixtures, at which the extreme swelling of elastomers is expected, are given in Table 6.2.2.

Table 6.2.2. Position of a maximum on the swelling curve of crosslinked elastomers in binary mixtures. [Adapted, by permission, from V. V. Tereshatov, M. I. Balashova, A. I. Gemuev, Prediction and regulating of properties of polymeric materials, *Ural Branch of AS USSR Press*, Sverdlovsk, 1989, p. 3.]

Elastomer	Binary mixture	Components ratio, wt%	
		Calculation	Experiment
PEU	toluene-acetone	90/10	90/10
	cyclohexanone-acetone	40/60	50/50
	heptane-acetone	30/70	25/25
PBU	decane-DBP	30/70	30/70
	TO-DBP	40/60	40/60
	DOS-DBP	60/40	50/50
SCN-26	ethyl acetate-1,4-dioxane	-	-
	ethyl acetate-acetone	70/30	70/30
	toluene-acetone	70/30	70/30

Results of calculation of the liquid phase composition at maximum swelling of elastomer correlate with the experimental data (see Table 6.2.2). The approach predicts the existence of an extremum on the swelling curve. This increases the forecasting efficiency of the prediction.

The application of "approximation of the uniform liquid" (AUL) for prediction of extreme swelling of crosslinked elastomers is proven under condition of coincidence of composition of a two-component solvent in a liquid phase and in the swollen elastomer. Results of study of total and selective sorption by crosslinked elastomers of components of SLs are given below.[3]

Crosslinked PBU [(v_e/V_0) = 0.20 kmol/m^3] and crosslinked elastomer of butadiene-nitrile rubber SCN-26 [(v_e/V_0) = 0.07 kmol/m^3] were used in this study. The tests were carried out at 25±0.10°C in the following mixtures: n-nonane-tributyl phosphate (TBP), n-hexane-dibutyl phthalate (DBP), n-hexane-dibutyl maleate (DBM), and dioctyl sebacate (DOS)-diethyl phthalate (DEP). A crosslinked elastomer SCN-26 was immersed to equilibrate in amyl acetate-dimethyl phthalate mixture. Liquid phase composition was in range of 5 to 10%. A sol-fraction of samples (plates of 0.9×10^{-2} m diameter and in 0.3×10^{-2} m thickness) was preliminary extracted with toluene.

For the high accuracy of the analysis of binary solvent composition, a volatile solvent, hexane, was used as a component of SL in most experiments. Following the attainment of equilibrium swelling, the samples were taken out of SL and held in air until the full evaporation of hexane, that was controlled by constant mass of sample. A content of a nonvolatile component of SL in elastomer was determined by the difference between the amount of liq-

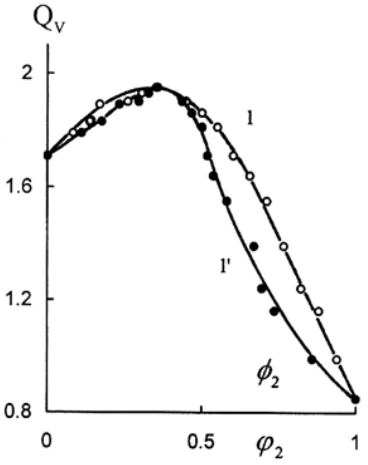

Figure 6.2.5. Dependence of equilibrium swelling of PBU on the φ_2 value for DEP in the liquid phase (1) and the ϕ_2 value inside the gel (1') swollen in the mixture DOS-DEP.

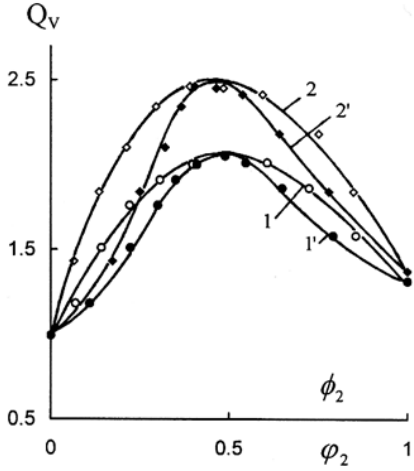

Figure 6.2.6. Dependence of equilibrium swelling of PBU on the φ_2 value for DEP in the liquid phase (curves 1 and 2) and the ϕ_2 value inside the swollen gel (curves 1' and 2') in the mixtures: 1,1'-hexane(1)-DBM(2), 2,2'- hexane(1)-DBP(2).

uid in the swollen sample and the amount of hexane evaporated. In the case of SL with non-volatile components (such as, DBP or DOS) the ratio of SL components in the swollen PBU was determined by the gas-liquid chromatography, for which purpose toluene extract was used.

The volume fractions of components 1 and 2 of SL in a liquid phase φ_1 and φ_2 were calculated on the basis of their molar ratio and densities ρ_1 and ρ_2.

Volume fraction of polymer, υ_3, in the swollen sample was calculated from the equation:

$$\upsilon_3 = \frac{1}{Q_V + 1}$$

where:

Q_V volume equilibrium swelling of elastomer in SL.

Volume fractions φ_1 and φ_2 of components 1 and 2 of low-molecular-mass liquids inside the swollen gel were determined from the equation:

$$\phi_i = \frac{\upsilon_i}{1-\upsilon_3}, \quad (i = 12)$$

where:

ϕ_i volume fraction of i-component related to the total volume of its low-molecular-mass part (not to the total volume of three-component system)

The results of study of sorption of two-component liquids in PBU and in crosslinked elastomer SCN-26 are shown in Figures 6.2.5-6.2.8, as dependencies of Q_V on the volume

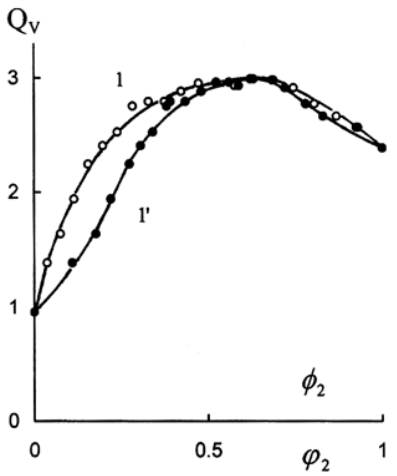

Figure 6.2.7. Dependence of equilibrium swelling of PBU on the φ_2 value for TBP in the liquid phase (1) and the ϕ_2 value in the gel (1') swollen in the mixture: nonane-TBP.

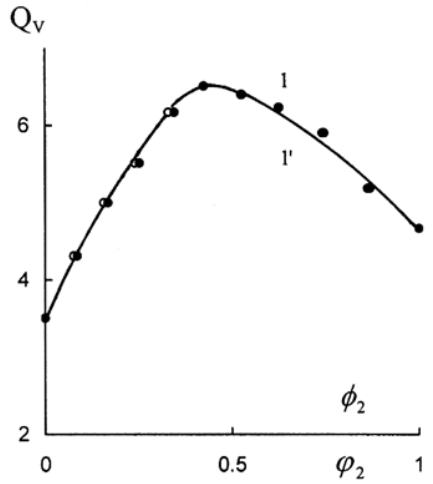

Figure 6.2.8. Dependence of equilibrium swelling of crosslinked elastomer SCN-26 on the φ_2 value for DMP in the liquid phase (1) and the ϕ_2 value in the gel (1'), swollen in the mixture: amyl acetate-DMP.

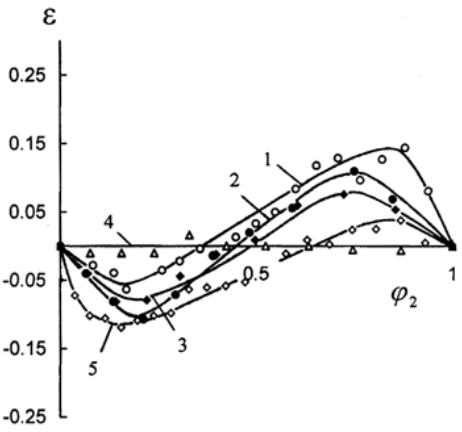

Figure 6.2.9. Experimental dependence of the preferential sorption ε on the volume fraction φ_2 of component 2 in the liquid phase: 1-DOS(1)-DEP(2)-PBU(3), 2-hexane(1)-DBP(2)-PBU(3), 3-hexane(1)-DBM(2)-PBU(3), 4-amyl acetate(1)-DMP(2)-SCN-26(3), 5-nonane(1) -TBP(2)-PBU(3).

fraction φ_2 of component 2 in a liquid phase and on the volume fraction ϕ_2 of component 2 of SL that is a part of the swollen gel. The data vividly show that extremum swelling of crosslinked elastomers in SL can be observed in all investigated cases. At the maximum value of Q_V, the compositions of SL in the liquid phase and in the swollen elastomer practically coincide ($\varphi_2 \approx \phi_2$).

The total sorption can be determined by the total content of the mixed solvent in the swollen skin[9] or in the swollen elastic network (these results). The dependencies of Q_V on φ_2 (Figures 6.2.5-6.2.8) reveal the influence of liquid phase composition on the total sorption. The total sorption of the binary solvent by polymer can also be measured by the value of the volume fraction of polymer in the swollen gel[9] because the value of υ_3 is unequally related to the volume fraction of the absorbed liquid, $\upsilon_3 = 1-(\upsilon_1 + \upsilon_2)$. At the fixed total sorption (Q_V or υ_3 = const) the preferential sorption, ε, can be found from the following equation:

$$\varepsilon = \phi_1 - \varphi_1 = \varphi_2 - \phi_2$$

At the same values of Q_v difference between coordinates on the abscissa axes of points of the curves 1-1', 2-2' (Figures 6.2.5-6.2.8) are equal ε (Figure 6.2.9).

As expected,[10] preferential sorption was observed, with the essential distinction of molar volumes V_1 and V_2 of components of the mixed solvent (hexane-DBP, DOS-DEP). For swelling of the crosslinked elastomer SCN-26 in the mixture of components, having similar molar volumes V_1 and V_2 (e.g., amyl acetate-dimethyl phthalate) the preferential sorption of components of SL is practically absent. Influence of V_1 and V_2 and the influence of double interaction parameters on the sorption of binary liquids by crosslinked elastomers was examined by the method of mathematical experiment. Therewith the set of equations describing swelling of crosslinked elastomers in binary mixture, similar to the equations obtained by Bristow[6] from the Flory-Rehner theory[11] and from the work of Schulz and Flory,[12] were used:

$$\ln\varphi_1 + (1-l)\varphi_2 + \chi_{12}\varphi_2^2 = \ln\upsilon_1 + (1-l)\upsilon_2 + \upsilon_3 + \chi_{12}\upsilon_2^2 + \chi_{12}\upsilon_3^2 +$$

$$+(\chi_{12} + \chi_{13} - l\chi_{23})\upsilon_2\upsilon_3 + (\nu_e / V_3)V_1\left(\upsilon_3^{1/3} - \frac{2}{f}\upsilon_3\right) \qquad [6.2.6]$$

$$\ln\varphi_2 + \left(1-l^{-1}\right)\varphi_1 + l^{-1}\chi_{12}\varphi_1^2 = \ln\upsilon_2 + \left(1-l^{-1}\right)\upsilon_1 + \upsilon_3 + l^{-1}$$

$$\left[\chi_{12}\upsilon_1^2 + l\chi_{23}\upsilon_3^2 + (\chi_{12} + l\chi_{23} - \chi_{13})\upsilon_1\upsilon_3\right] + (\nu_e / V_3)V_2\left[\upsilon_3^{1/3} - \frac{2}{f}\upsilon_3\right] \qquad [6.2.7]$$

where:

l $= V_1/V_2$

f functionality of a network

The analysis of calculations from Eqs. [6.2.6] and [6.2.7] has shown that if $V_1 < V_2$, the preferential sorption is promoted by difference in parameters of interaction, when $\chi_{12} > \chi_{13}$. The greater is χ_{12} value at $V_1 \neq V_2$ the more likely preferential sorption takes place with all other parameters being equal. The same applies to the diluted polymer solutions.

To improve calculations of the preferential sorption in the diluted solutions of polymers, the correction of Flory's theory is given in works[9,13-15] by introduction of the parameter of three-component interaction, χ_T, into the expression for free energy of mixing, and substitution of χ_T by q_T.[14] This approach is an essential advancement in the analysis of a sorption of two-component liquids by polymer. On the other hand, the increase in the number of experimental parameters complicates the task of prediction of the preferential sorption.

In swelling crosslinked elastomers, the preferential sorption corresponds to the maximum Q_V value and compositions in a swollen polymer and a liquid phase practically coincide (Figures 6.2.5-6.2.8). This observation can be successfully used for an approximate evaluation of the preferential sorption.

Assuming that $\varphi_1 = \phi_1$ and $\varphi_2 = \phi_2$ at extremum of the total sorption ($\phi_3 = \phi_3^{min}$), AUL[5] can be used to calculate the effective value of χ_{12}^e from the expression for χ_{123}:[16]

$$\chi_{12}^e = \frac{\chi_{13}}{\varphi_2^m} + \frac{\chi_{23}V_1}{\varphi_1^m V_2} - \frac{\chi_{123}^m V_1}{V_{12}^m \varphi_1^m \varphi_2^m} \qquad [6.2.8]$$

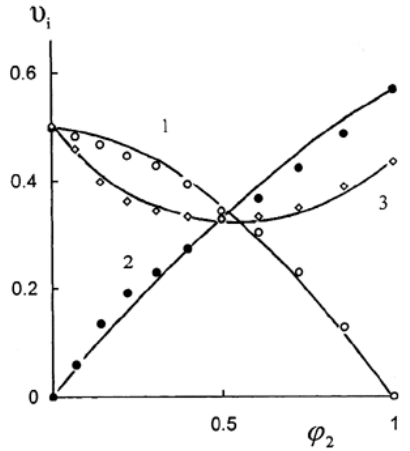

Figure 6.2.10. Experimental data and calculated dependence of equilibrium fraction of components υ_1 (1), υ_2 (2), and υ_3 (3) in PBU sample swollen in the hexane-DBP mixture on the φ_2 value for DBP in the liquid phase: lines - calculation, points - experimental.

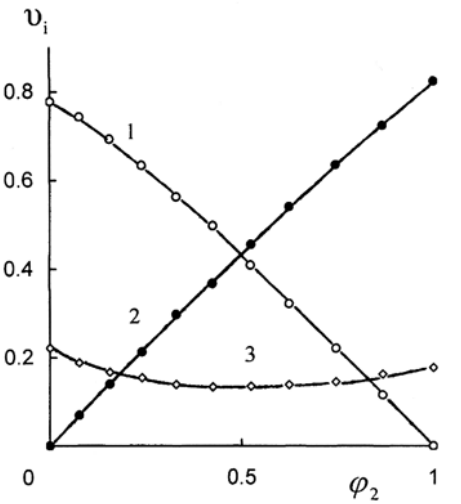

Figure 6.2.11. Dependence of equilibrium fraction of components υ_1 (1), υ_2 (2), and υ_3 (3) in SCN-26 sample swollen in the amyl acetate-DMP mixture on the φ_2 value for DMP in the liquid phase: lines - calculation, points - experimental.

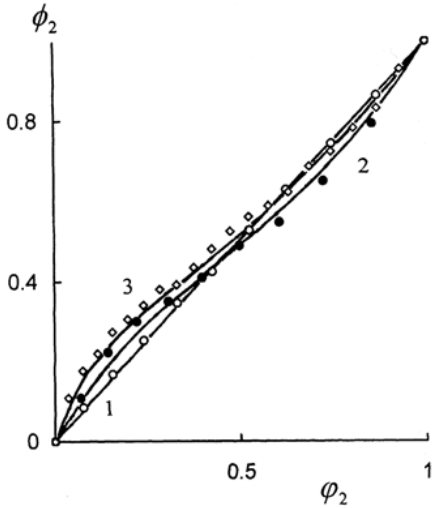

Figure 6.2.12. Dependence of equilibrium ϕ_2 value on the φ_2 value in the liquid phase: 1-amyl acetate (1)-DMP (2)-SCN-26(3), 2-hexane(1)-DBM(2)-PBU (3), 3-nonane(1)-TBP(2)- PBU (3); lines - calculation, points - experimental.

where:

m	the index for the maximum of sorption.
χ^e_{12}	the value, calculated from the equation [6.2.8], substitutes χ_{12} from the Eqs. [6.2.6] and [6.2.7]

The results of calculations are presented as dependencies of volume fractions, υ_1, υ_2, and υ_3 of the triple system components (swollen polymer) vs. the volume fraction φ_2 (or φ_1) of the corresponding components of the liquid phase (Figures 6.2.10 and 6.2.11). For practical purposes it is convenient to represent the preferential sorption as the dependence of equilibrium composition of a binary liquid (a part of the swollen gel) vs. composition of the liquid phase. These calculated dependencies (solid lines) and experimental (points) data for three systems are given in Figure 6.2.12. The results of calculations based on AUL, are in the satisfactory agreement with experimental data.

Hence the experimentally determined equality of concentrations of SL components in the swollen gel and in the liquid phase allows one to predict composition of liquid, whereby polymer swelling is at its maximum, and the preferential sorption of components of SL. To refine dependencies of ϕ_1 on φ_1 or ϕ_2 on φ_2, correction can be used, for example, minimization of the square-law deviation of calculated and experimental data on the total

sorption of SL by polymer. Thus it is necessary to account for proximity of the compositions of solvent in the swollen gel and the liquid phase.

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6.3 SWELLING DATA ON CROSSLINKED POLYMERS IN SOLVENTS

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Data on equilibrium swelling of selected crosslinked elastomers in different solvents are presented in Table 6.3.2. All data were obtained in the author's laboratory during the last 5 years. The network density values for these elastomers are given in Table 6.3.1.

The data can be used for the quantitative evaluation of thermodynamic compatibility of solvents with elastomers and for calculation of ΔZ, the thermodynamic interaction parameter. These data can be recalculated to the network density distinguished by the network density value, given in Table 6.3.1, using Eq. [4.2.9]. Network density values can be used for the calculation of the interaction parameter. It should be noted that each rubber has specific ratio for the equilibrium swelling values in various solvents. This can help to identify rubber in polymeric material.

Temperature influences swelling (see Subchapter 4.2). Equilibrium swelling data at four different temperatures are given in Table 6.3.3.

Polymer samples were made from industrial rubbers. The following polyols were used for preparation of polyurethanes: butadiene diol (M~2000) for PBU, polyoxybutylene glycol (M~1000) for SCU-PFL, polyoxypropylene triol (M~5000) for Laprol 5003, polydiethylene glycol adipate (M~2000) for P-9A and polydiethylene glycol adipate (M~800) for PDA. Polyurethanes from these polyols were synthesized by reaction with 2,4-toluylene diisocyanate with addition of crosslinking agent - trimetylol propane, PDUE, synthesized by reaction of oligobutadiene isoprene diol (M~4500) with double excess of 2,4-toluylene diisocyanate, followed by the reaction with glycidol.

Table 6.3.1. Network density values for tested elastomers (data obtained from the elasticity modulus of samples swollen in good solvents)

Elastomer	Trade mark	Network density, (kmol/m^3)×10^2
Silicone rubber	SCT	6.0
Butyl rubber	BR	8.9
Polybutadiene rubber	SCDL	40.5
Ethylene-propylene rubber	SCEPT	2.7
Isoprene rubber	SCI-NL	8.9
Butadiene-nitrile rubber	SCN-26	5.1
Polydiene-urethane-epoxide	PDUE	16.0
Polybutadiene urethane	PBU	20.8
Polyoxybutylene glycol urethane	PFU	10.0
Polyoxypropylene glycol urethane	Laprol 5003	43.0
Polydiethylene glycol adipate urethane	P-9A	6.4
Polydiethylene glycol adipate urethane	PDA	9.6

Table 6.3.2 Equilibrium swelling data (wt%) at 25°C

Solvent\elastomer	SCT	BR	SCDL	SCEPT	SCI -NL	SCN -26	PDUE	PBU	SCU -PFL	Laprol	P-9A	PDA
Hydrocarbons												
Pentane	355		75		214							
Hexane	380	305	105	586	300		122	78	16	44	4	
Heptane	367	357		881		10	137	84	16	42	0	
Isooctane	380	341					101			32	0	
Decane		391		1020		7	139			28	1	
Cyclohexane		677				155	315		39			3
Transformer oil	47		230	1580	600	24	238		3	53	4	0.5
Toluene		384		1294		435	492	356	134	315	77	31
Benzene		233		511		506	479	359	158	340	175	73
o-Xylene		515					496	356	122	288	53	42
Ethers												
Diamyl	310		220	889	584	20	248			87	2	

Solvent\elastomer	SCT	BR	SCDL	SCEPT	SCI -NL	SCN -26	PDUE	PBU	SCU -PFL	Laprol	P-9A	PDA
Diisoamyl	333								33			3
Didecyl				791		7	168			22	2	
Dioctyl	120	428	180	896	702	11	203		6	41	0.1	1
Diethyl of diethylene glycol	85		156		242					251		54
1,4-Dioxane		23						264	178		782	
Tetrahydrofuran								48	192		848	
Esters of monoacids												
Heptyl propionate	260	236	304	382		287						
Ethyl acetate		20					170		133		213	88
Butyl acetate		55		55		562	317	251	121		64	40
Isobutyl acetate		48					267	210		238	48	35
Amyl acetate		82					343			249	36	
Isoamyl acetate		74						236	100			22
Heptyl acetate				213				545	100			6
Methyl capronate							369	285	115	260	36	26
Isobutyl isobuturate							328	276	64		6	6
Esters of multifunctional acids												
Dihexyl oxalate				28		350			73	166	11	9
Diethyl phthalate				6		837	47	93	165	272	496	126
Dibutyl phthalate				9		767	123	154	121	228	47	20
Dihexyl phthalate						570				187	9	
Diheptyl phthalate									37			3
Dioctyl phthalate	8			28			189		29			1
Dinonyl phthalate							211	181	33			1.4
Didecyl phthalate									23			0.5
Diamyl maleate						425	197		71	232	19	14
Dimethyl adipate						560				246	716	6
Diamyl adipate							294	203	88			
Dihexyl adipate						280					8	
Dioctyl adipate							295	199	42		2	2
Dipropyl sebacate				20					126		12	0.6

Solvent\elastomer	SCT	BR	SCDL	SCEPT	SCI -NL	SCN -26	PDUE	PBU	SCU -PFL	Laprol	P-9A	PDA
Diamyl sebacate									70			2
Diheptyl sebacate				60						118	3	
Dioctyl sebacate	13		160	127	445	39	261	162	5.5	74	0.4	0.7
Triacetyne						34		15	28		489	129
Tricresyl phosphate						800	45		140			80
Tributyl phosphate							300	244	238	256	93	105
Ketones												
Cyclohexanone							577			327	523	
Acetone				7			44		88		218	99
Alcohols												
Ethanol									49			16
Butanol								25	72		7	12
Pentanol							28	33	66		10	5
Hexanol							46	34	62		9	4
Heptanol								36	67		19	
Nonanol									57			3
Halogen compounds												
CCl_4				2830		284	999			584	66	
Chlorobenzene									234		277	114
Chloroform								1565	572			616
Fluorobenzene									205			113
Nitrogen compounds												
Diethyl aniline								336	120			34
Dimethylformamide								52			918	
Nitrobenzene							277	298	242	377	799	241
Capronitrile						769	142		115		84	
Acetonitrile						47	69	16			323	
Aniline									317			423

Table 6.3.3 Equilibrium swelling data (wt%) at -35,-10, 25, and 50°C

Solvent\Elastomer	Laprol*	SCU-PFL	P-9A	PBU	SCN-26
Isopropanol	8,12,37,305	8,19,72,-	8,10,18,28	3,5,18,28	20,23,26,41

Solvent\Elastomer	Laprol*	SCU-PFL	P-9A	PBU	SCN-26
Pentanol	27,34,80,119	16,25,78,104	7,9,10,18	8,9,33,52	31,37,49,60
Acetone	80,366,381,-	80,122,132,-	48,73,218,-	56,321,347,-	162,254,269,382
Ethyl acetate	214,230,288,314	113,114,133,138	209,210,210,213	165,171,187,257	324,343,395,407
Butyl acetate	294,304,309,469	119,122,123,125	41,44,64,80	288,293,307,473	404,426,518,536
Isobutyl acetate	259,259,288,-	89,92,100,105	23,28,48,57	210,212,223,348	309,326,357,362
Amyl acetate	315,309,315,426	124,136,144,155	16,18,36,44	285,297,298,364	343,347,358,359
Tetrahydrofuran	91,96,97,119	119,177,192,-	838,840,848,859	45,51,57,80	145,150,166,-
o-Xylene	363,368,389,471	117,121,122,137	24,25,53,60	328,357,369,375	428,440,405,406
Chlorobenzene	522,537,562,-	241,242,242,246	238,244,277,333	517,528,559,698	967,973,985,1256
Acetonitrile	19,21,28,33	23,26,39,41	254,263,323,362	6,10,16,27	47,47,47,82
Hexane	50,52,61,75	2,3,9,14	4,4,4,28	51,56,63,80	-
Toluene	360,366,380, 397	120,122,134,149	50,57,77,85	331,339,372,415	-

*$(\nu_e/V) = 0.149$ kmol/m^3. Network density values for other elastomers correspond to Table 6.3.2

6.4 INFLUENCE OF STRUCTURE ON EQUILIBRIUM SWELLING

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Swelling of single-phase elastomers is, other parameters being equal, limited by the chemical network. Microphase separation of hard and soft blocks can essentially influence swelling of block-copolymers. Hard domains formed in this process are knots of physical network, which can be resistant to action of solvents.[1-4] Swelling of polyurethane block-copolymers with urethane-urea hard segments is investigated. The maximum values of swelling, Q^{max}, of segmented polyurethane (prepolymer of oligopropylene diol with functional isocyanate groups) cured by 4,4'-methylene-bis-o-chloroaniline (MOCA) are given in Tables 6.4.1 and 6.4.2. The prepolymer Vibratane B 600 was obtained by the reaction of oligopropylene diol with 2,4-toluylene diisocyanate. The swelling experiments were carried out in four groups of solvents of different polarity and chemical structure.[5] The effective molecular mass of elastically active chains, M_c, between network crosslinks was estimated from the Flory-Rehner equation.[6] The interaction parameter of solvent with polymer was determined by calculation.

In the first variant of calculation, a classical method based on the solubility parameter concept, was used with application of Bristow and Watson's semi-empirical relationship for χ_1:[7]

$$\chi_1 = \chi_1^S + \left(\frac{V_1}{RT}\right)\left(\delta_1 - \delta_p\right)^2 \qquad [6.4.1]$$

where:

- χ_1^S a lattice constant whose value can be taken as 0.34
- V_1 the molar volume of the solvent
- R_1 the gas constant
- T the absolute temperature
- δ_1 and δ_p the solubility parameters of the solvent and the polymer, respectively

However, to evaluate χ_1 from Eq. [6.4.1], we need accurate data for δ_1.

In some cases the negative M_c values are obtained (Tables 6.4.1, 6.4.2). The reason is that the real values of the entropy component of the χ_1 parameter can strongly differ from the 0.34 value.

Table 6.4.1. Characteristics of polyurethane-solvent systems at 25°C. [Adapted, by permission, from U.S. Aithal, T.M. Aminabhavi, R.H. Balundgi, and S.S. Shukla, *JMS - Rev. Macromol. Chem. Phys.*, 30C (1), 43 (1990).]

Penetrant	Q^{max}	χ_1	M_C
Monocyclic aromatics			
Benzene	0.71	0.378	630
Toluene	0.602	0.454	790
p-Xylene	0.497	0.510	815
Mesitylene	0.402	0.531	704
Chlorobenzene	1.055	0.347	905
Bromobenzene	1.475	0.347	1248
o-Dichlorobenzene	1.314	0.357	1106
Anisole	0.803	0.367	821
Nitrobenzene	1.063	0.356	835
Aliphatic alcohols			
Methanol	0.249	1.925	-90
Ethanol	0.334	0.349	172
n-Propanol	0.380	0.421	484
Isopropanol	0.238	0.352	249
n-Butanol	0.473	2.702	-131
2-Butanol	0.333	1.652	-307
2-Methyl-1-propanol	0.389	0.440	535
Isoamyl alcohol	0.414	0.357	398

Table 6.4.2. Characteristics of polyurethane-solvent systems at 25°C. [Adapted, by permission, from U.S. Aithal, T.M. Aminabhavi, R.H. Balundgi, and S.S. Shukla, *JMS - Rev. Macromol. Chem. Phys*., 30C (1), 43 (1990).]

Penetrant	Q^{max}	χ_1	M_C
Halogenated aliphatics			
Chloroform	4.206	0.362	3839
Bromoform	5.583	0.435	4694
1,2-Dibromoethane	1.855	0.412	770
1,3-Dibromopropane	1.552	0.444	870
Dichloromethane	2.104	0.34	1179
Trichloroethylene	1.696	0.364	1098
Tetrachlorethylene	0.832	0.368	429
1,2-Dichlorethane	1.273	0.345	728
Carbon tetrachloride	1.058	0.538	860
1,4-Dichlorobutane	0.775	0.348	626
1,1,2,2- Tetrachloroethane	5.214	0.34	6179
Miscellaneous liquids			
Methyl acetate	0.494	0.341	370
Ethyl acetate	0.509	0.422	513
Ethyl benzoate	0.907	0.34	1111
Methyl ethyl ketone	1.261	0.364	2088
Tetrahydrofuran	2.915	0.39	2890
1,4-Dioxane	2.267	0.376	2966
DMF	1.687	1.093	-1184
DMSO	0.890	1.034	-975
Acetonitrile	0.184	0.772	182
Nitromethane	0.302	1.160	5734
Nitroethane	0.463	0.578	382
n-Hexane	0.069	1.62	2192
Cyclohexane	0.176	0.753	287
Benzyl alcohol	4.221		

In the second variant of evaluation of M_c, data on the temperature dependence of volume fraction of polymer, φ_2, in the swollen gel were used. Results of calculations of M_c from the Flory-Rehner equation in some cases also gave negative values. The evaluation of

M_c in the framework of this approach is not an independent way, and M_c is an adjustment parameter, as is the parameter χ_1 of interaction between solvent and polymer.

In the last decades of evaluation of the physical network density of SPU was done on samples swollen to equilibrium in two solvents.[2,9,10] Swelling of SPU in toluene practically does not affect hard domains.[9,11] Swelling of SPU (based on oligoethers diol) in a tributyl phosphate (a strong acceptor of protons) results in full destruction of the physical network with hard domains.[2] The effective network density was evaluated for samples swollen to equilibrium in toluene according to the Cluff-Gladding method.[12] Samples were swollen to equilibrium in TBP and the density of the physical network was determined from equation:[2,10]

$$(v_e / V_0)_{dx} - (v_e / V_0)_x = (v_e / V_0)_d \qquad [6.4.2]$$

As the result of unequal influence of solvents on the physical network of SPU, the values of effective density of networks calculated for the "dry" cut sample can essentially differ. The examples of such influence of solvents are given in the work.[2] SPU samples with oligodiene soft segments and various concentration of urethane-urea hard blocks were swollen to equilibrium in toluene, methyl ethyl ketone (MEK), tetrahydrofuran (THF), 1,4-dioxane and TBP (experiments 1-6, 9, 10, 12). SPU based on oligoether (experiment 7), with urethane-urea hard segments, and crosslinked single-phase polyurethanes (PU) on the base of oligodiene prepolymer with functional isocyanate groups, cured by oligoether triols (experiments 8, 11) were also used. The effective network densities of materials swollen in these solvents were evaluated by the Cluff-Gladding method through the elasticity equilibrium modulus. The data are given in Table 6.4.3 per unit of initial volume.

The data shows that the lowest values of the network density are obtained for samples swollen to equilibrium in TBP. Only TBP completely breaks down domains of hard blocks. If solvents which are acceptors of protons (MEK, THF, 1,4-dioxane) are used in swelling experiment an intermediate values are obtained between those for toluene and TBP.

The network densities of SPU (experiments 8 and 11) obtained for samples swollen in toluene, TBP, 1,4-dioxane and THF coincide (Table 6.4.3).[2]

Table 6.4.3. Results of the evaluation of equilibrium swelling and network parameters of PUE. [Adapted, by permission, from E.N. Tereshatova, V.V. Tereshatov, V.P. Begishev, and M.A. Makarova, *Vysokomol . Soed.*, 34B, 22 (1992).]

#	ρ kg/m³	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)
		Toluene		THF		MEK		1,4-Dioxane		TBP	
1	996	1.56	1.03	0.46	0.77	1.08	0.41	3.76	0.12	5.12	0.06
2	986	2.09	0.53	0.52	0.43	1.40	0.23	6.22	0.04	11.15	0.02
3	999	1.74	0.77	0.49	0.73	1.11	0.38	7.88	0.03	18.48	0.01
4	1001	2.41	0.44	0.49		1.75	0.13	14.3	0.02	∞	
5	1003	4.46	0.15	0.47		3.29		∞		∞	
6	984	2.63	0.40	0.57	0.39	1.45	0.19	3.44	0.14	4.21	0.08
7	1140	0.86	1.83	2.06		1.40	0.73	1.86	0.31	7.22	0.04

#	ρ kg/m³	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)	Q_V	(v_e/V_0)
		Toluene		THF		MEK		1,4-Dioxane		TBP	
8	972	2.42	0.35	1.84	0.36	1.01	0.54	2.08	0.34	1.48	0.35
9	979	2.26	0.39	1.72	0.37	0.98	0.54	1.97	0.35	1.62	0.31
10	990	2.00	0.63	0.47		0.99	0.55	2.42	0.29	2.19	0.24
11	991	4.11	0.18	2.79	0.18	3.98	0.17	3.42	0.18	2.54	0.17
12	997	2.42	0.50	1.00	0.32	2.68	0.12	4.06	0.13	4.32	0.08

(v_e/V_0), kmol/m³

To understand the restrictions to swelling of SPU caused by the physical network containing hard domains, the following experiments were carried out. Segmented polybutadiene urethane urea (PBUU) on the base of oligobutadiene diol urethane prepolymer with functional NCO-groups ($M \approx 2400$), cured with MOCA, and SPU-10 based on prepolymer cured with the mixture of MOCA and oligopropylene triol ($M \approx 5000$) were used. The chemical network densities of PBUU and SPU were 0.05 and 0.08 kmol/m³, respectively. The physical network density of initial sample, $(v_e/V_0)_d$, of PBUU was 0.99 kmol/m³ and of SPU-10 was 0.43 kmol/m³.

Samples of PBUU and SPU-10 were swollen to equilibrium in solvents of different polarity: dioctyl sebacate (DOS), dioctyl adipate (DOA), dihexyl phthalate (DHP), transformer oil (TM), nitrile of oleic acid (NOA), dibutyl carbitol formal (DBCF), and tributyl phosphate (TBP).

The values of equilibrium swelling of elastomers in these solvents, Q_1, (ratio of the solvent mass to the mass of the unswollen sample) are given in Table 6.4.4. After swelling in a given solvent, samples were swollen in toluene to equilibrium. The obtained data for swelling in toluene, Q_V^T, indicate that the physical networks of PBUU and SPU-10 do not change on swelling in most solvents. Equilibrium swelling in toluene of initial sample and the sample previously swollen in other solvents is practically identical. Several other observations were made from swelling experiments, including sequential application of different solvents. If preliminary disruption of the physical network of PBUU and SPU-10 by TBP occurs, swelling of these materials in toluene strongly increases. Similarly, samples previously swollen in TBP have higher equilibrium swelling, Q_2, when swollen in other solvents. The value of Q_2 is likely higher than equilibrium swelling Q_1 of initial sample (Table 6.4.4). Q_2 for PBUU is closer to the value of equilibrium swelling of a single-phase crosslinked polybutadiene urethane, PBU, having chemical network density, $(v_e/V_0)_x = 0.04$ kmol/m³. Thus, the dense physical network of polyurethane essentially limits the extent of equilibrium swelling in solvents, which do not breakdown the domain structure of a material.

Table 6.4.4. Equilibrium swelling of SPBUU and SPU-10 (the initial sample and sample after breakdown of hard domains by TBP) and swelling of amorphous PBU at 25°C

Solvent	SPBUU			SPU-10			PBU
	Initial structure		After breakdown of domains	Initial structure		After breakdown of domains	
	Q_1	Q^T	Q_2	Q_1	Q^T	Q_2	Q_3
-		1.35			2.10		
DOS	0.62	1.34	3.97	0.66	2.09	3.04	5.56
DOA	0.68	1.34	4.18	0.84	2.05	3.26	
DBP	0.60	1.36	3.24	0.90	2.12	3.38	
DHP	0.63	1.34	3.71	0.85	2.10	3.22	4.47
TO	0.57	1.35	2.29	0.58	2.07	1.92	1.99
NOA	0.59	1.36	4.03	0.72	2.10	2.86	4.66
DBCP	0.69	1.37	4.60	0.155	2.96	3.45	5.08
TBP	5.01	7.92*	5.01	4.22	5.43	4.22	

* The result refers to the elastomer, having physical network completely disrupted

Swelling of SPU can be influenced by changes in elastomer structure resulting from mechanical action. At higher tensile strains of SPU, a successive breakdown of hard domains as well as micro-segregation may come into play causing reorganization.[13-15] If the structural changes in segmented elastomers are accompanied by breakdown of hard domains and a concomitant transformation of a certain amount of hard segments into a soft polymeric matrix or pulling of some soft blocks (structural defects) out of the hard domains,[14] variation of network parameters, is inevitable. It is known[4] that high strains applied to SPU causes disruption of the physical network and a significant drop in its density.

The data of equilibrium swelling of SPU-1 with oligodiene soft segments obtained by curing prepolymer by the mixture of MOCA and oligobutadiene diol ($M \approx 2000$) with the molar ratio 1/1 are given in Table 6.4.5. The initial density of the SPU-1 network $(v_e/V_0)_{dx}$ = 0.206 kmol/m^3, the physical network density $(v_e/V_0)_d$ = 0.170 kmol/m^3. After stretching by 700 % and subsequent unloading, the value $(v_e/V_0)_{dx}$ = 0.115 kmol/m^3 and $(v_e/V_0)_d$ = 0.079 kmol/m^3. The density of the chemical network $(v_e/V_0)_x$ = 0.036 kmol/m^3 did not change. Samples were swollen to equilibrium in a set of solvents: toluene, n-octane, cyclohexane, p-xylene, butyl acetate, DBCF, DBP, DHP, dihexyl sebacate (DHS), DOA and DOS (the values of density, ρ_1, and molar volume of solvents, V_1, are given in Table 6.2.5).

The data in Table 6.4.5 shows that, after stretching, the volume equilibrium swelling of samples does not change in DBCF.[4] In other solvents equilibrium swelling is noticeably increased.

Swelling experiments of samples previously swollen in solvents and subsequently in toluene have shown that the value of equilibrium swelling in toluene varies only for samples previously swollen in DBCF. The effective network densities evaluated for SPU-1 samples, swollen in DBCF, and then in toluene, have appeared equal (0.036 and 0.037 kmol/m^3, respectively) and these values correspond to the value of the chemical network parameter,

$(v_e/V_0)_x$, of SPU-1. It means that DBCF breaks down the physical network of elastomer; thus, the values of Q_v in DBCF do not depend on the tensile strain. In all other cases, swelling of SPU-1 in toluene differs only marginally from the initial swelling of respective samples in toluene alone. Therefore, these solvents are unable to cause the breakdown of the physical network.

Table 6.4.5. Equilibrium swelling of SPU-1 samples in various solvents before and after stretching at 25°C (calculated and experimental data). [Adapted, by permission, from V.V. Tereshatov, Vysokomol. soed., 37A, 1529 (1995).]

Solvent	ρ_1, kg/m^3	$V_1\times10^3$, m^3/kmol	Q_V (ε=0)	χ_1 (ε=0)	Q_V (ε=700%)		Q_V^T (ε=700%)	Q_V^T (ε=0)
					calc	exp		
Toluene	862	107	3.54	0.32	5.06	4.87		
DBP	1043	266	1.12	0.56	1.47	1.53	4.85	3.49
n-Octane	698	164	0.79	0.75	0.90	0.93	4.94	3.60
Cyclohexane	774	109	1.46	0.60	1.78	1.95	4.99	3.63
p-Xylene	858	124	2.94	0.36	4.17	3.93	4.81	3.52
Butyl acetate	876	133	2.28	0.44	3.13	2.97	5.12	3.69
DOS	912	468	1.21	0.38	1.60	1.71	5.10	3.63
DOA	924	402	1.49	0.32	2.19	2.18	5.00	3.61
DHS	923	340	1.74	0.30	2.55	2.44	5.01	3.59
DHP	1001	334	1.25	0.47	1.71	1.74	4.79	3.47
DBCP	976	347	4.48			4.51	9.92	9.98

The calculation of equilibrium swelling of SPU-1 (after its deformation up to 700 % and subsequent unloading) in a given solvent was carried out using the Flory - Rehner equation. In our calculations we used values of the χ_1 parameter of interaction between solvents and elastomer calculated from experimental data of equilibrium swelling of initial sample (ε=0) in these solvents.

The diference between calculated and experimental data on equilibrium swelling of SPU-1 samples after their deformation does not exceed 9%. Therefore, the increase in swelling of SPU-1 is not related to the change of the χ_1 parameter but it is related to a decrease in the $(v_e/V_0)_{dx}$ value of its three-dimensional network, caused by restructure of material by effect of strain.

The change of the domain structure of SPU exposed to increased temperature (~200°C) and consequent storage of an elastomer at room temperature may also cause a change in equilibrium swelling of material.[16]

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