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Activity Coefficients of the Low-Molecular-Mass Components in Swelling Polymers

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Abstract—Solutions in which low-molecular-mass substances and a swelling polymer form a homogeneous system have been studied. A method for predicting the activity and osmotic coefficients during variation in the solute concentration has been proposed. The dependence of the osmotic coefficients on the solution concentration, in conjunction with volumetric changes in the system and the swelling pressure, has been analyzed.

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Polymer solutions in low-molecular-mass substances (LMMSs) are fairly well understood because the preparation and processing of polymers into composite materials and other products commonly involve polymer solutions [1, 2].

Typically, the first step of dissolution of a polymer is the swelling of the polymer. Swelling is defined as unidirectional mixing where the polymer plays the role of a solvent and the substance (vapor or liquid) in which it swells acts as a solute. A distinction is made between limited and unlimited swelling [1]. The LMMS and the swelling polymer form a homogeneous two-component system without changing the aggregate state of the polymer [3]. The solid aggregate state of the polymer corresponds to three phase states: crystalline, liquid-crystalline, and amorphous [1, 4, 5]. Of these three states, only polymers in an amorphous glassy or rubberlike state produce a homogeneous solution with an LMMS [6–9]. In this solution, the polymer acts as a solvent of the LMMS.

An LMMS can be in the initial liquid state or in the form of a vapor. In the first case, the state of the polymer solution is represented by a constitutional diagram [6, 7]; in the second case, the state of the polymer solution is represented by an absorption isotherm. Depending on the solution concentration, the state of the polymer can transition from the initial glassy state to a rubberlike, viscous-flow state. This feature has been shown, for example, in studies of the state of polymer solutions via the NMR method [10–12], the bimodal sorption theory [13], the Lindström–Laatikainen model [14], etc. At the same time, the formation of the solution is accompanied by ambiguous changes in the volume of the system caused by osmotic effects (swelling pressure) [1]. These effects and the great difference in the size of the solution components lead to a significant deviation of the properties of polymer solutions from the properties of ideal solutions. The degree of deviation from ideal behavior [1] is expressed in terms of excess changes in the thermodynamic functions,

$$\Psi^E = \Psi^M - \Psi^i, \quad (1)$$

where $\Psi^M = \Delta\Psi^M$ and $\Psi^i = \Delta\Psi^i$ are the thermodynamic functions of formation of a real and ideal solution, respectively, and in terms of activity and osmotic coefficients [15] in the equation for chemical potential μ_i of the solution components:

$$\overline{\mu_i} = \mu_i^0 + RT\ln x_i y_i = \mu_i^0 + RTg_i \ln x_i, \quad (2)$$

$$g_i - 1 = \ln\gamma_i / \ln x_i. \quad (3)$$

Here, γ_i and g_i are the activity and osmotic coefficients at a molar fraction of the component of x_i. The composition of the solution can additionally be expressed in terms of other concentration units (volume and mass fraction, molality, etc.); in this case, the activity-coefficient magnitudes change [15].

During the formation of the solution, the polymer cannot transition into the gas phase, whereas the LMMS can. This feature significantly facilitates the experimental determination of activity coefficients in the study of the polymer solution–LMMS vapor equilibrium. In a close approximation, it is assumed that the vapor is in the state of an ideal gas; hence, at equilibrium for the LMMS in the gas and solid phases, the equality of the respective chemical potentials must be fulfilled:

$$\Delta\mu_1^{\Gamma} = \overline{\Delta\mu_1}. \quad (4)$$

Assuming that a liquid pure sorbate is a reference state, we obtain

$$RT \ln P/P_0 = RT \ln a_1, \quad (5)$$

where activity a_1 of the LMMS can be described as the product of the LMMS concentration in the polymer solution and the activity coefficient.

The activity-coefficient method is fairly informative because the $\gamma_1(x_1)$ dependence can be used to characterize the class of the resulting solution [15] and, in polymer systems, the osmotic coefficient is directly related to the actual swelling pressure [15–17]. However, this method has been described in the literature to a significantly lesser extent [2, 16, 17] than the method of excess thermodynamic functions.

In this context, the aim of this study is to analyze the dependence of osmotic coefficients, swelling pressure, and volume of the system on the polymer solution concentration.

EXPERIMENTAL

Samples of commercial viscose (a degree of polymerization of 370, a density of 1.50 g/cm^3) and polyamide fibers (anid, i.e., poly(hexamethylene adipamide), a molecular mass of 25×10^3 to 28×10^3, a density of 1.13 g/cm^3) were used in the study. Before the experiment, the fibers were washed free from lubricating substances in acetone. Structured gelatin films (a density of 1.39 g/cm^3) were prepared with the use of 7% solutions in water with formalin (0.01 kg per kg gelatin). Films with thicknesses of 20–40 μm were cast onto a poly(methyl methacrylate) substrate and then dried in the air and in vacuum at a temperature of 60°C. Films of PIB ($M = 1.5 \times 10^6$, a density of 0.93 g/cm^3) were prepared via pouring of a PIB solution in toluene onto a glass substrate and subsequent drying in air and in vacuum at 60°C.

The equilibrium vapor pressure of the LMMS and the polymer solution concentration were determined with a high-vacuum McBain balance. The constants of the quartz springs were 2–4 mg/mm. The elongations of the springs during sorption were measured with a KM-4 cathetometer with a precision of ±0.005 mm. The mass of a sample was 100–150 mg. The volume of the system—cartridges with springs and samples, connecting lines, and an additional vessel to maintain constant pressure in kinetic measurements—was ~0.008 m^3. The stepwise feeding of the LMMS vapor into this large volume of the system and the small samples provided an initial increase in the pressure to the "planned" value and a subsequent slight decrease in it during the sorption of the vapor by the samples. Equilibrium pressure was established within 3–7 days at each point of the isotherm. The equilibrium concentration of the LMMS in the polymer solution was calculated in terms of the mass gain of the polymer, which was measured with the quartz balance in the vacuum system per initial mass of the pure polymer.

Volume measurements of the polymer during sorption were conducted by pycnometry and hydrostatic weighing on a Mohr–Westphal balance. The pycnometric media used in these methods were liquids that do not cause polymer swelling: heptane for the viscose and polyamide fibers and the gelatin films and water for PIB. Changes in the volumes of the film materials were determined simultaneously with the sorption isotherm via the use of a volumetric setup at the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences. In this setup, changes in the volume of a sample were recorded with a differential transformer, whose core was tightly bound to the surface of the polymer. A detailed description of the dilatometer is given in [18]. The results of these measurements and the pycnometric studies were almost the same.

RESULTS AND DISCUSSION

The chemical potential of an LMMS in a polymer solution (Eqs. (4), (5)) can be expressed in terms of the absorption isotherm equation. In [19–21], the high descriptive ability of the equation of the theoretical probabilistic model of sorption was given:

$$\theta = \exp(-(-\Delta\mu_1^{\Gamma}/E)^n), \quad (6)$$

where $\theta = m/m_0$ is the relative LMMS concentration in the polymer solution; m and m_0 are the molality (mol LMMS/1000 g polymer) at relative partial pressures of the LMMS above the solution P and P_0; P_0 is the saturated vapor pressure at temperature T; E is the characteristic absorption energy; and constant n is associated with the type of polymer: $n = 0.7$ and 0.5 for glassy polymers and elastomers, respectively, and $n \cong 1/3$ for sorbate-soluble polymers. These n values correspond to the Tager classification [1] for characteristic types of vapor-absorption isotherms for polymers, which are shown in Fig. 1. At the state of equilibrium, from Eqs. (4) and (6), we have the expression for variation in the chemical potential of the LMMS in the polymer solution:

$$\overline{\Delta\mu_1} = \Delta\mu_1^{\Gamma} = -E\left(-\ln\theta\right)^{1/n}. \quad (7)$$

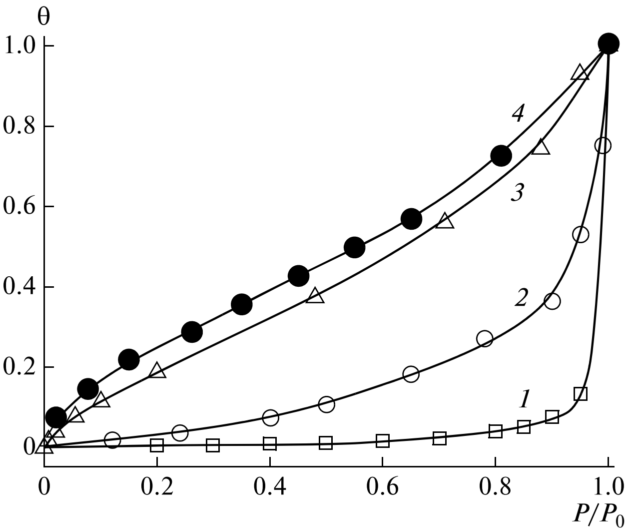

Fig. 1. Isotherms of the absorption of (*1, 3, 4*) water and (*2*) heptane by (*1*) polyacrylic acid ($M = 7 \times 10^4$), (*2*) polyisobutylene, (*3*) viscose fibers, and (*4*) gelatin. The points denote the experiment; the curves, calculations according to Eq. (6) at n = (*1*) 1/3, (*2*) 0.5, and (*3, 4*) 0.7.

The mole fraction of the LMMS in the solution in Eq. (2) is defined, as in the osmotic theory of adsorption [16], as $\theta = m/m_0$, while the nonideality of the solution is expressed in terms of the osmotic coefficient:

$$\Delta\overline{\mu_1} = gRT\ln\theta. \tag{8}$$

The activity- and osmotic-coefficient values depend on the mode of expression of concentration [15, 22, 23]; therefore, the representation of concentration in the form of θ is quite acceptable.

From Eqs. (7) and (8), we obtain the expression for the osmotic coefficient:

$$g = \frac{E}{RT}\left(\ln\frac{1}{\theta}\right)^{\frac{1}{n}-1} = \left(\frac{E}{RT}\right)^n\left(\ln\frac{P_0}{P}\right)^{1-n}. \tag{9}$$

Before switching to the consideration of the osmotic effects in polymer systems and the bulk deformation or sorbostriction [24] at the swelling-polymer–vapor equilibrium, let us discuss the relevance of the made assumptions.

It has been noted above that, at $n \approx 0.3$, Eq. (6) describes the vapor sorption by sorbate-soluble polymers. Therefore, it can be assumed that the isotherm equation holds true for the mutually soluble LMMS solution–vapor equilibrium. For these systems, the activity coefficients are given, for example, in [23]; in addition, concentrations are typically measured in mole fractions x_i or molalities m_i, which are related as follows:

$$m_A = \frac{x_A \cdot 1000}{(1-x_A)M_B}, \tag{10}$$

where subscripts A and B describe the A and B components. Expressing the variation in the chemical potential of a liquid solution component in terms of x_i, we obtain

$$\Delta\overline{\mu_i} = RT\ln\gamma_i x_i. \tag{11}$$

Here, γ_i is the activity coefficient of the *i*th component.

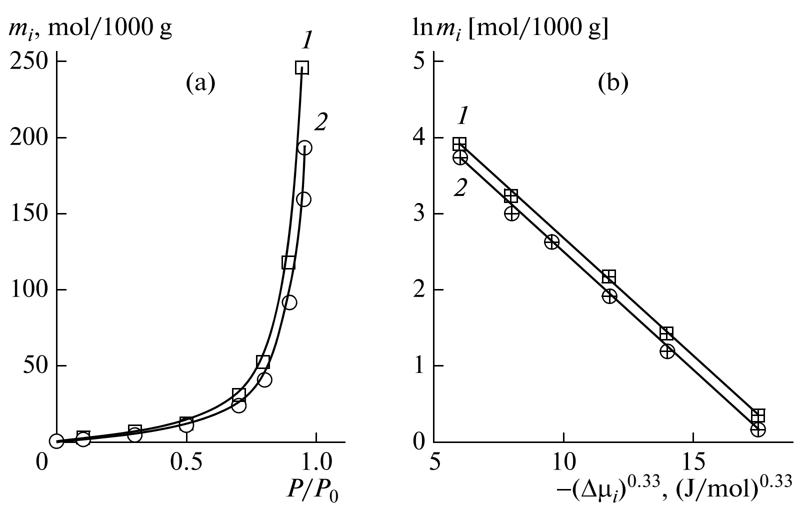

Fig. 2. Sorption isotherms in (a) $m(P/P_0)$ and (b) $\ln m_i\,((-\Delta\mu_i)^{0.33})$ coordinates for the dichloroethane–benzene system at T = 293 K: (*1*) dichloroethane and (*2*) benzene.

Activity coefficients in the $C_2H_5OH{-}H_2O$ and $H_2O{-}H_2SO_4$

$h(C_2H_5OH)$	$\gamma(C_2H_5OH)$	$\gamma^*(C_2H_5OH)$ [23]	$h(H_2O)$	$\gamma(H_2O)$	$\gamma^*(H_2O)$	$h(H_2O)$	$\gamma(H_2O)$	$\gamma^*(H_2O)$ [23]
$C_2H_5OH{-}H_2O$						$H_2SO_4{-}H_2O$		
0.302	3.38	3.02	0.957	1.02	1.01	0.856	0.96	0.90
0.453	2.29	2.26	0.912	1.03	1.01	0.613	0.69	0.68
0.688	1.20	1.15	0.858	1.08	1.07	0.372	0.42	0.44
0.754	1.11	1.08	0.818	1.15	1.17	0.202	0.26	0.25
0.822	1.05	1.03	0.650	1.61	1.62	0.100	0.13	0.13
0.917	1.01	1.02	0.586	1.92	1.78	0.0045	0.06	0.06
0.984	1.008	1.004	0.406	2.46	2.03	0.020	0.03	0.03

$h = P/P_0$.

From Eqs. (2) and (7), we have

$$RT\ln\gamma_i x_i = -E(-\ln\theta)^{1/n}, \quad (12)$$

$$\ln\gamma_{ix} = -\frac{E}{RT}(-\ln\theta)^{1/n} - \ln x_i, \quad (13)$$

where $\theta = m/m_0$ and m_0 is the parameter of the isotherm in $\ln m = f(\Delta\mu_1)^{0.33}$ coordinates at $P/P_0 = 1$.

The dichloroethane–benzene system is nearly ideal. The isotherms in $m(P/P_0)$ and $\ln_i((-\Delta\mu_i)^{0.33})$ coordinates are shown in Fig. 2. The behavior of the system is satisfactorily approximated by Eq. (6) at $n = 0.33$, $E_{av} = 16.4$ J/mol, m_0 (dichloroethane) = 1054 mol/1000 g C_6H_6, and m_0 (C_6H_6) = 1340 mol/1000 g dichloroethane. The γ_{ix} coefficients calculated from Eq. (13) are given below.

x_i	0.1	0.3	0.5	0.7	0.8	0.9	0.95
$\gamma(C_6H_6)$	1.08	1.08	1.01	0.99	0.99	1.01	1.02
γ(dichloroethane)	1.15	1.09	1.02	0.99	0.99	1.01	1.02

It is evident that the activity coefficients are close to unity.

Nonideal solutions include the $C_2H_5OH{-}H_2O$ and $H_2SO_4{-}H_2O$ systems. Data on the activity coefficients of the components of these systems are given in [23]; the solution–vapor equilibrium isotherms are shown in Fig. 3. The isotherms satisfactorily obey Eq. (6) at the following values of the constants: $n = 0.33$, $m_0(C_2H_5OH)$ = 17150 mol/1000 g H_2O, $m_0(H_2O)$ = 4920 mol/1000 g C_2H_5OH, and E_{av} = 5.5 J/mol for the $C_2H_5OH{-}H_2O$ system and $n = 0.28$, $m_0 = 652$ mol/1000 g, and $E = 108$ J/mol for the $H_2O{-}H_2SO_4$ system. The calculated and experimental activity coefficients of the components are shown in the table. Here, the calculation according to Eq. (13) and the data from [23] are likewise in satisfactory agreement.

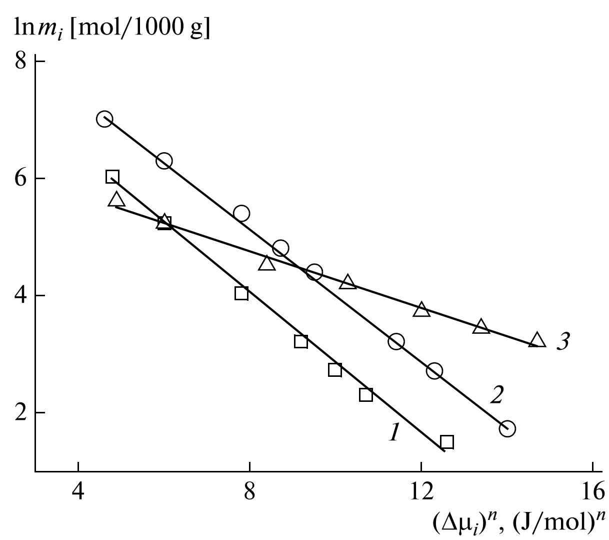

Fig. 3. Sorption isotherms for the $H_2O{-}C_2H_5OH$ and $H_2O{-}H_2SO_4$ systems: (*1, 3*) H_2O and (*2*) C_2H_5OH.

Thus, the above-described method for determining the activity coefficients gives fairly correct results.

A swelling pressure, which is an actual pressure caused by LMMS molecules, acts in a polymer system, unlike in the discussed solutions. This pressure is a hydrostatic pressure that acts inside the system and is always positive in sign; it tends to stretch the system, i.e., cause a positive strain.

The "stretching" of the polymer matrix is accompanied by an increase in the oppositely directed force; in terms of the macroscopic model of the system, this force can be represented as an elastic force of the springs tending to compress the system; in terms of the molecular model, it is determined by a decrease in the configuration entropy during the stretching of the polymer chains. At equilibrium, the oppositely directed forces compensate each other to establish an equilibrium internal pressure in the system, which is commonly referred to as swelling pressure π.

Swelling pressure can be determined through a few approaches, which yield the same result. Consider a polymer solution (hereinafter, primed) separated from pure LMMS vapor (double primed) by the surface of the swelling polymer permeable only to the LLMS. In terms of thermodynamics, the processes of osmosis [15] and swelling are similar; however, in the first case (dilute polymer solutions), semipermeable membranes are required to form an interface between the liquid solution and the solvent (although the properties of the membrane are disregarded in thermodynamic calculations). In the second case, the interface is the intrinsic surface of the swelling polymer whose macromolecules, owing to their large sizes and the presence of an intermolecular entanglement network, intermolecular bonds, crystallites, and other factors, cannot leave their phase and do not require additional constructions in the form of a membrane.

At equilibrium, the chemical potentials of the LMMS in the two phases are equal:

$$\mu_1' = \mu_1'', \tag{14}$$

$$\mu_1' = \mu_1^0(P', T) + g\ln x_1, \tag{15}$$

$$\mu_1'' = \mu_1^0(P'', T) + RT\ln P_1/P_1^0. \tag{16}$$

If $P' = P''$, then

$$\ln P_1/P_1^0 = g\ln x_1. \tag{17}$$

This result was used above to determine the osmotic coefficient in liquid solutions.

The formation of a solution in a solid aggregate state leads to the occurrence of an internal pressure, which is referred to as swelling pressure:

$$\pi = P' - P''. \tag{18}$$

To find this pressure, the chemical potentials at pressures P' and P'' are expressed in terms of compressibility factor χ_1 [15]:

$$\mu_1' = \mu_1^0(T) + P'V_1^0(T_1, O)\left(1 - \frac{1}{2}\chi_1 P'\right) + gRT\ln x_1, \tag{19}$$

$$\mu_1'' = \mu_1^0(T) + P''V_1^0(T_1, O)\left(1 - \frac{1}{2}\chi_1 P''\right) + RT\ln P/P_0, \tag{20}$$

where $V_1^0(T_1,O)$ is the molar volume of the LMMS extrapolated to zero pressure. Denoting the molar volume of the pure LMMS at a pressure of 0.5 ($P'' + P'$) in terms of $\overline{V_1^0}$, equating μ_1' and μ_1'', and using the equality $x_1 = \theta$, we obtain

$$\pi\overline{V_1^0} = RT\ln P/P_0 - gRT\ln\theta. \tag{21}$$

Consider the variation in the osmotic coefficient in polymer solutions. Elastomer systems include the PIB–heptane system (m_0 = 5.5 mol/1000 g, E = 324 J/mol) (Figs. 1, 4). During the dissolution of a nonpolar LMMS by a nonpolar elastomer, dispersion interactions are dominant, the sorption process is associated with an increase in the combinatorial component of entropy, and the osmotic coefficients are less than unity. In this case, bulk strains are always positive because a polymer limited to elastic walls undergoes free swelling and the swelling pressure is lower than ideal and decreases to a negative internal pressure attributed to the energy of intermolecular interactions of macromolecules that hinder the transition of the polymer in the viscous-flow state.

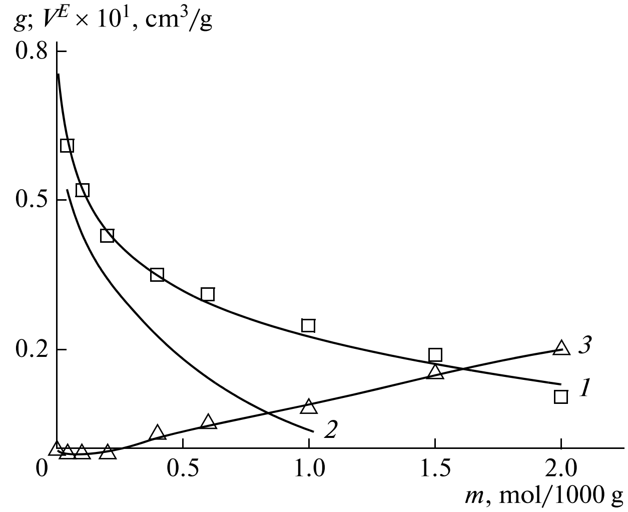

Fig. 4. Variation in osmotic coefficients (*1*) g and (*2*) g_φ calculated according to Eqs. (9) and (25) and (*3*) in the excess volume in the PIB–heptane system. The points denote the experimental data.

It is of interest to compare the derived data with the predictions of the Flory–Huggins theory [1], according to which

$$\Delta\mu_1 = RT\ln a_1 = RT[\ln\varphi_1 + (1-\varphi_1) + \chi_1(1-\varphi_1)^2] \tag{22}$$

for the polymer phase and

$$\overline{\Delta\mu_1} = RT\ln\gamma_\varphi\varphi_1 = RTg_\varphi\ln\varphi_1. \tag{23}$$

Hence, we obtain

$$\ln\gamma_\varphi = (1-\varphi_1) + \chi_1(1-\varphi_1)^2; \tag{24}$$

$$g_\varphi = [\ln\varphi_1 + (1-\varphi_1) + \chi_1(1-\varphi_1)^2]/\ln\varphi_1. \tag{25}$$

Heptane is a poor solvent for PIB because the constant calculated from the sorption isotherm is $\chi_1 \approx 1.5$. It is evident from Fig. 4 that g_φ varies similarly to osmotic coefficient g calculated according to Eq. (9). For these systems, excess volume V^E must be positive.

For the benzene–natural rubber system, $\chi_1 = 0.4$ ($n = 0.30$; $E = 16.2$ J/mol, and $a_0 = 9.97$ g/g); that is, benzene is close to an ideal solvent ($\chi_1 = 0.5$). However, as in the previous system, $g_\varphi < 1$ and activity coef-

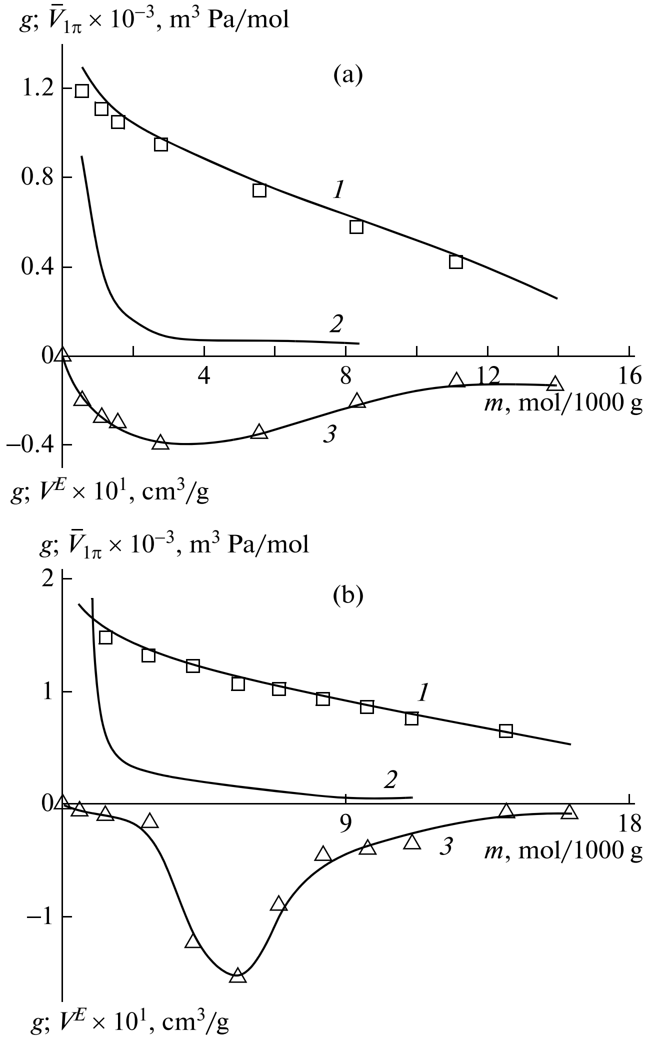

Fig. 5. Variations in (*1*) the osmotic coefficient and (*2*) the osmotic potential calculated according to Eqs. (9) and (21) and (*3*) in the excess volume in (a) the viscose fiber–water and (b) gelatin–water systems. The points denote the experimental data.

ficient γ_φ approaches unity only upon the transition of the system to a viscous-flow state ($\varphi_1 \to 1$).

φ_1	0.2	0.4	0.6	0.8	0.9	0.98
γ_φ	2.96	2.07	1.57	1.24	1.10	1.02
g_φ	0.92	0.21	0.12	0.036	0.095	0.019

The most complicated case is polar glassy-polymer–water systems, where the noncombinatorial interaction resulting in the formation of hydrogen bonds is dominant.

Negative and positive bulk strains for the gelatin films and the cellulose fibers during the sorption of water vapor are shown in Fig. 5. Similar results were obtained for PVA, polyamide and ion-exchange fibers based on PAN, and wool fibers [25]. Figures 4 and 5 suggest that the experimental osmotic coefficients and the values calculated according to Eq. (9) satisfactorily correspond to each other.

Negative strains (compression of samples relative to their initial state) are consistent with the fact that $g > 1$; that is, the intermolecular forces, while maintaining the glassy state of the polymer, seemingly play the role of a "rigid wall" that compresses the polymer–sorbate system. In this case, the "depth" of the negative strains is proportional to the energy of intermolecular interactions expressed in terms of the integral heat of sorption, q_i, which is 135, 85, and 21 kJ/kg for gelatin, cellulose, and anid polyamide fibers, respectively.

Under the effect of the sorbate, when the polymer is still in a glassy state, some characteristics of the system, such as the elastic modulus, are capable not only of remaining constant but also of increasing. One of the explanations for this is the fact that the sorbate molecules that actively interact with the polymer chain units with an energy higher than the energy at which the units interact with each other cause a kind of a physicochemical "crosslinking" of the polymer, which contributes to the polymer compaction and, hence, increases in the strength and elastic modulus of the polymer system. This feature corresponds to negative excess volumes of the system, V^E (Fig. 5). Similar negative bulk strains during initial sorption are observed in "rigid" microporous adsorbents, even in the case of sorption of inert gases [24, 26].

The initial portion ($g > 1$) for cellulose and polyamides is consistent with the NMR data [10–12]. Here, the lowest values of the spin–spin relaxation times of the adsorbed-water protons are recorded; this fact corresponds to both the hydrogen bonding of the water molecules with one of the OH groups of cellulose or the NH group of polyamides and bridging between the active groups of the neighboring macromolecules. This bridging can lead to the compression of the system (the antiplasticization effect), i.e., to an increase in the total pressure within the system relative to that of an ideal system ($g > 1$), rather than to positive changes in the volume. This assumption is confirmed by the calculation of the osmotic potential according to Eq. (21); the variation in this parameter is shown in Fig. 5.

Minimum bulk strains and the beginning of an increase in the system volume approximately correspond to $g = 1$, the inflection of the equilibrium curve, and sharp decreases in the $\bar{V}_{1\pi}$ value and relaxation time T_1. In the vicinity of the inflection of the $g(\theta)$ curve, the g value undergoes a further dramatic decrease, which simultaneously corresponds to the transition of the samples from a glassy state to a rubberlike state [9, 13]. This process is additionally consistent with the beginning of clustering of the water molecules [14], a decrease in the spin–lattice relaxation times [10–12], and the approaching of the sorbate structure to the bulk phase.

Thus, the nonideality of solutions in which the swelling polymer acts as a solvent of the LMMS can be quantitatively estimated through excess thermodynamic functions and activity or osmotic coefficients. Techniques for the calculation of activity coefficients and their variation with a change in the polymer solution concentration in elastomer and glassy polymer systems have been proposed. The relationship between the bulk strain of a solution of a low-molecular-mass liquid in a swelling polymer and the change in the osmotic coefficients has been shown.

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