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Thermodynamics of dissolution of glassy polymers

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Abstract

A parametric semi-empirical thermodynamic theory for the dissolution of glassy polymers in liquids is formulated based on the experimental results on Gibbs energy, enthalpy and entropy of mixing in isothermal conditions for a large number of systems. The values of these thermodynamic functions include the contribution from the glassy structure of the polymer, which depends on the volume fraction of metastable voids, the cohesion energy of polymer, and the entropy depression parameter. The glassy-state contribution to the enthalpy and entropy of mixing is large and negative, which provides sufficient difference from the same functions for the elastic polymers. However, this also leads to the enthalpy/entropy compensation, and the values of Gibbs energy of mixing only weakly depend on the glassy nature of the polymer. The theory is shown to provide adequate explanation for all specific features of the concentration dependences of different thermodynamic functions found in experiment at constant temperature. The parameters of the model are tabulated for a large variety of solutions of polymer glasses. © 2002 Published by Elsevier Science Ltd.

Keywords: Dissolution of glassy polymers; Enthalpy; Entropy

1. Introduction

Being cooled below the glass transition temperature, the polymer exists in a metastable form of a glassy liquid. It is characterized by the same amorphous structure as the elastic polymer, but the segmental motions are frozen, and no conformational rearrangements of the macromolecular chain can occur. The apparent reason for the glass formation is kinetic. The polymer segment consists of the several monomer units and forms a large number of intermolecular bonds with its surroundings which have to be rearranged while the conformation of the chain is changing. Hence, the activation energy of such process is large, and the thermal molecular motion will not be able to provide it below the certain temperature (T_g). Theoretical approach based on the kinetic viewpoint was developed by Volkenstein and Ptitsin [1], Hirai and Eyring [2], Wunderlich et al. [3]. The main idea was that the molecular motion was provided by the free volume, which was considered to be formed by the voids in the liquid structure which were in the dynamic equilibrium with the molecules. The number of voids in the liquid and the activation energy of their formation were the parameters of the theory.

However, the glass transition of the polymer is not exclusively a kinetic process. The very early works of Bekkendahl [4,5] revealed the distinct changes in the thermodynamic properties of polymers during the glass transition. On the temperature scans of the specific heat and the thermal expansion coefficient there were found discontinuities, which resembled the features of the second order phase transition. That formed the background of the thermodynamic theory of glass formation which was introduced by Gibbs and DiMarzio [6]. They analyzed the configurational entropy of the polymer chain on a lattice with energetically unequivalent orientations of segments in the presence of voids, and found out that at a certain temperature the configurational entropy became zero which was considered to be the thermodynamic glass transition—the second order phase transition. The kinetic glass formation occurred ca. 50 K above that temperature.

Meanwhile, the thermodynamic approach to the properties of polymer glasses is of the major practical importance as well. The large number of polymers and their compositions (plastics) are used exclusively in the glassy state. One can distinguish two main approaches in the thermodynamics of polymer glasses. The first is the detailed analysis of the temperature dependence of the thermal properties of polymers, e.g. heat capacity, thermal expansion, heat conductivity, etc. Much experimental work on that was carried out by Wunderlich and Baur [7]. In the last decade, the influence of annealing and physical ageing on the heat capacity and the

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enthalpy relaxation of polymer glass was extensively studied by Cowie, Ferguson and McEwen [8,9]. The obtained results found adequate theoretical explanation in various multiparameter theories [10–13].

The second approach corresponds to the isothermal thermodynamic properties of the compositions of the glassy polymers with solvents and various industrial liquids, and deals with the compatibility and the interactions between the components in such mixtures. The values of Gibbs energy, enthalpy and entropy of mixing and their concentration dependence at constant temperature are of the major interest. The present work is devoted to the problems, which arise concerning the latter aspect of the thermodynamics of polymer glasses.

The first experimental studies on the isothermal thermodynamics of dissolution of polymer glasses were performed in the early 1950s. The enthalpy of dissolution of polymethylmethacrylate (PMMA) and polystyrene (PS) in different solvents was measured by Schulz and Hellfritz [14], Jenkel and Gorke [15], and Tager and Kargin [16]. The vapor sorption studies on PS were carried out by Bawn et al. [17]. Later the large number of works were carried out by Tager and Adamova [18–21]. The main conclusions of the experimental research might be summarized as follows [18]:

(A) The isothermal process of dissolution of glassy polymer may be considered as quasi-equilibrium. Although the thermodynamic functions of the process depend on the pretreatment of the polymer, this influence is reproducible and does not dominate over intermolecular interactions in the solution.

(B) The enthalpy of mixing of glassy polymer with any solvent is always negative, no matter of its quality. This is considered to be the specific influence of the glassy nature. Thus the enthalpy of mixing ΔH^{m} is assumed consisting of two terms [18]

$$\Delta H^{\mathrm{m}} = \Delta H_{\mathrm{int}} + \Delta H_{\mathrm{g}} \qquad (1)$$

where ΔH_{int} depends on intermolecular interactions between components and can be of any sign, ΔH_{g} is the contribution from the glassy state of the polymer. During the process of dissolution the chains of glassy polymer become flexible under the influence of a solvent. Since the glass possesses excess enthalpy over the elastomer, this process is accompanied with enthalpy relaxation and evolution of heat. Some empirical approaches of the evaluation of ΔH_{g} were introduced [15].

(C) Gibbs energy of mixing of glassy polymers with solvents is close to that for the elastic polymers. The entropy of mixing has rather large negative values despite the quality of the solvent. There is no adequate interpretation of these features.

The existing experimental results show a definite influence of the glassy nature of the polymer on the isothermal thermodynamic functions of mixing with solvents. The rigorous consideration of this influence would be made on the basis of the general theory for the glassy state. However, the latter is far from being accomplished. Hence, as a first step, it seems reasonable to consider the influence of the glassy state being the additional contribution to the expressions for the isothermal thermodynamic functions of elastomer solutions obtained in the well-known lattice [22] or equation-of-state [23] models.

We believe that in the first approximation this can be done by means of a rather simple parametric lattice model using as adjustable parameters the most common set for the theories of the glassy state, i.e. the number (concentration) of voids in the system and the cohesion energy of polymer (energy of void formation). Of course, both parameters are, in fact, implicit functions of temperature, external pressure and the kinetics of the process. In order to study the principal possibility of such approximation, here we restrict the consideration to the case of the practical importance in experimental thermodynamics of dissolution of polymers—equilibrium solutions at constant temperature and normal pressure.

Thus, the objective of the present work was to develop a relatively easy parametric thermodynamic approach to the thermodynamics of dissolution of polymer glasses correctly interpreting the experimental results obtained by the authors for the various systems over the long period of time.

2. The parametric model

Consider a bulk polymer below its glass transition temperature. It has an amorphous metastable structure characterized by excess enthalpy and volume over hypothetical equilibrium elastic polymer at this temperature. Let φ_{v}^{0} be the volume fraction of metastable voids in the structure. Note that φ_{v}^{0} corresponds only to the excess free volume which is provided by the nature of glass but not to the overall free volume of the polymer.

When a solvent is added to the glassy polymer, the process of plasticization occurs which eventually tends to the complete dissolution of the polymer. There are two possibilities for a solvent molecule intruding into the glassy structure. First, it may separate the segments of the polymer chains and interact with them. Second, it may occupy the metastable void in the glassy structure. We suppose the latter process corresponds to the plasticization of the polymer glass.

Let us calculate the enthalpy of mixing of a solvent with the glassy polymer at constant pressure. For the sake of simplicity, we use the well-known Guggenheim approach to regular solutions [24]. The energy of solution is

$$E = z\varepsilon_{12}n_1\varphi_2 + \tfrac{1}{2}z\varepsilon_{11}n_1\varphi_1 + \tfrac{1}{2}z\varepsilon_{22}n_2\varphi_2 - z\varepsilon_{22}n_{\mathrm{v}}$$

where ε_{12} is the adhesion energy, ε_{11} and ε_{22}, the cohesion energies of components, n_1 and φ_1, the number and the volume fraction of solvent molecules, n_2 and φ_2, the number

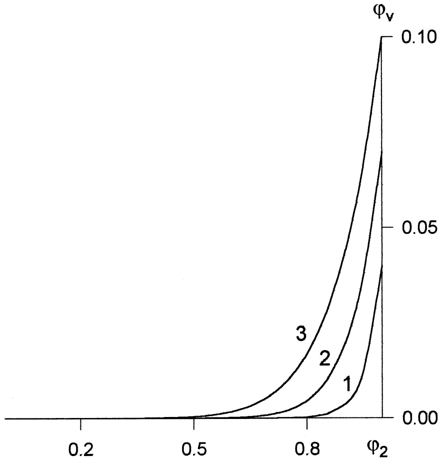

Fig. 1. Calculated concentration dependence of metastable voids volume fraction in the model solution of polymer glass; $\varphi_v^0 = 0.04$ (1), 0.07 (2), 0.1 (3).

and the volume fraction of monomer units, z, the coordination number of the equivalent lattice, and n_v is the number of metastable voids in the solution. The last term lowers the energy of solution due to the presence of metastable voids. The number of voids depends on the number of monomer units.

$$n_v = n_2\varphi_v$$

φ_v being the volume fraction of voids in solution related to the monomer units.

The energy values of pure components are:

$$E_1 = \tfrac{1}{2}z\varepsilon_{11}n_1 \qquad E_2 = \tfrac{1}{2}z\varepsilon_{22}n_2 - z\varepsilon_{22}n_2\varphi_v^0$$

Following the usual approach to the thermodynamics of condensed phases, we take the enthalpy of mixing being equal to the internal energy of mixing at constant pressure. However, the necessary adjustment can be easily done. Then the enthalpy of mixing per 1 mol of solution in Flory–Huggins notation will be

$$\Delta H^{\mathrm{m}} = \chi RT\varphi_1\varphi_2 + \varepsilon_{22}\varphi_2\left(\varphi_v^0 - \varphi_v\right) \qquad (2)$$

where χ is Flory–Huggins interaction parameter and here, ε_{22} refers to the whole monomer unit.

The first term in Eq. (2) corresponds to the interaction between solvent molecules and monomer units, the second term is the enthalpy change which stems from the process of occupying the metastable voids by solvent molecules.

Let us now estimate the volume fraction of metastable voids present in the solution (φ_v). Consider the plasticization process be a quasi-chemical reaction:

$$V + S = \alpha M + S \qquad (3)$$

In this notation V is a metastable void, S, the solvent molecule, and M is a monomer unit. This equation means that while a void is occupied by a solvent molecule, it disappears and αM ‘frozen’ monomer units ‘melt’. The equilibrium constant of reaction (3) is as follows:

$$K = \frac{\varphi_2^{\alpha}}{\varphi_2\varphi_v}$$

If $\varphi_2 = 1$, then $\varphi_v = \varphi_v^0$ which gives $K = 1/\varphi_v^0$, and

$$\varphi_v = \varphi_v^0\varphi_2^{\alpha-1} \qquad (4)$$

Parameter α which is the number of monomer units frozen by one metastable void might be defined as:

$$\alpha = \frac{1-\varphi_v^0}{\varphi_v^0} = \frac{1}{\varphi_v^0} - 1$$

Fig. 1 represents the calculated concentration dependence of the volume fraction of voids in the solution according to Eq. (4). One can see that the number of metastable voids rapidly decreases while a solvent is added to the glassy polymer.

Introducing Eq. (4) into Eq. (2) we finally obtain the enthalpy of mixing of the glassy polymer with a solvent:

$$\Delta H^{\mathrm{m}} = \chi RT\varphi_1\varphi_2 + \varepsilon_{22}\varphi_2\varphi_v^0\left(1 - \varphi_2^{(1/\varphi_v^0)-2}\right) \qquad (5)$$

Thus, taking into account Eq. (1) we get for the glassy-state contribution to the enthalpy of mixing:

$$\Delta H_{\mathrm{g}} = \varepsilon_{22}\varphi_2\varphi_v^0\left(1 - \varphi_2^{(1/\varphi_v^0)-2}\right) \qquad (6)$$

The value of ΔH_{g} depends on two parameters: the cohesion energy of polymer (ε_{22}) and the fraction of metastable voids (φ_v^0). As ε_{22} is always negative it determines the negative sign of ΔH_{g}. It is useful to note that Eq. (6) is not restricted to the regular solutions. For instance, the same form can be obtained in the framework of UNIQUAC model.

Using Eq. (6), one can easily obtain expressions for the glassy-state contribution to the enthalpy of infinite dilution and the partial enthalpy of the solvent which are widely used in the thermodynamics of polymer solutions:

$$\Delta H_{\mathrm{dil,g}} = \varepsilon_{22}\varphi_v^0\varphi_2^{(1/\varphi_v^0)-2} \qquad (7)$$

$$\Delta H_{1,\mathrm{g}} = \varepsilon_{22}\left(1 - \varphi_v^0\right)\varphi_2^{(1/\varphi_v^0)-1} \qquad (8)$$

The calculated concentration dependence of ΔH_{g}, $\Delta H_{\mathrm{dil,g}}$, $\Delta H_{1,\mathrm{g}}$ is presented in Fig. 2. One can see that all values are large and negative. The influence of glassy nature on $\Delta H_{\mathrm{dil,g}}$, $\Delta H_{1,\mathrm{g}}$ is restricted to concentrated solution where the metastable voids are still present in the structure of solution. However, since the enthalpy of mixing depends on the energy of pure components (including polymer glass), the contribution ΔH_{g} is significant over the entire concentration range.

While the reasons for the negative values of the enthalpy of mixing of the solutions of glassy polymers are quite clear, it is not so for the values of the entropy of mixing. The numerous experimental data, some of which will be discussed later, show the negative sign of ΔS^{m} for the solutions of glassy polymers. Since the combinatorial term

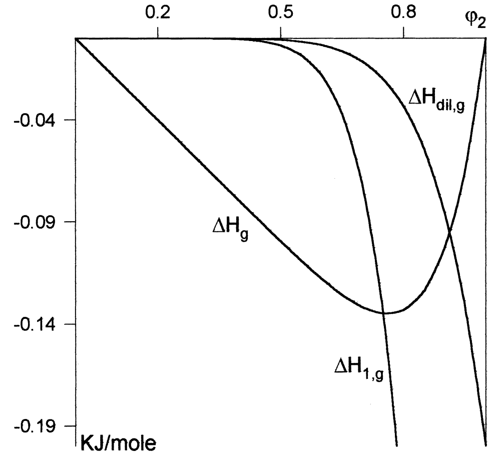

Fig. 2. Calculated concentration dependence of the glassy-state contribution to the enthalpy of mixing, enthalpy of dilution and excess partial enthalpy of a solvent in the model solution of polymer glass; $\varphi_v^0 = 0.1$, $\varepsilon_{22} = -2$ kJ/mol.

in the entropy of mixing is always positive, the observed values are strongly affected by the glassy nature of polymer. We may point out some possible contributions to ΔS^m which stem from the nature of glass. First, it is the change in conformational entropy of the chain during plasticization, which is likely positive. Second, it is the change in configurational entropy of the chain as defined by Gibbs and DiMarzio which is negative [8]. Third, there might be a contribution from the solvent. While penetrating to the glassy structure of the polymer, solvent molecules loose part of their translational entropy, which may be considered as the entropy of adsorption upon metastable voids. Since for now there is no adequate theory for such influence, let us introduce the glassy-state contribution to the entropy of mixing in the same parametric form as in Eq. (6):

$$\Delta S_g = s_{12}\varphi_2\varphi_v^0\left(1 - \varphi_2^{(1/\varphi_v^0)-2}\right) \tag{9}$$

Here, s_{12} is the entropy change per void which is the combination of aforesaid possible contributions. It will be shown further that in all studied cases s_{12} is negative and we may call it entropy depression parameter. Thus, the entropy of mixing in the solution of polymer glass without strong association is given by the combination of combinatorial entropy and Eq. (9):

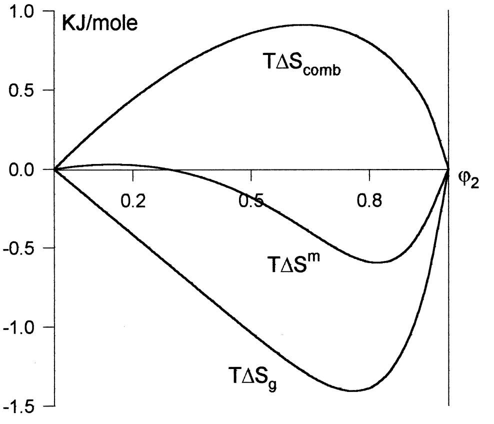

Fig. 3. Calculated concentration dependence of the entropy of mixing and its constituents in the model solution of polymer glass; $\varphi_v^0 = 0.1$, $s_{12} = -70$ J/mol K, $T = 298$ K.

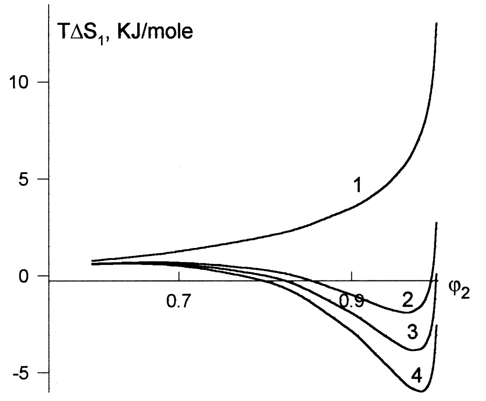

Fig. 4. Calculated concentration dependence of the excess partial entropy of a solvent in the model solution of elastomer (1) and polymer glass; $\varphi_v^0 = 0.1$, $s_{12} = -30$ (2), -40 (3), -50 (4) J/mol K, $T = 298$ K.

$$\Delta S^m = -R\left(x_1 \ln \varphi_1 + \frac{x_2}{p}\ln \varphi_2\right) + s_{12}\varphi_2\varphi_v^0\left(1 - \varphi_2^{(1/\varphi_v^0)-2}\right) \tag{10}$$

x_1 and x_2 are the molar fractions of solvent and monomer units in solution, p is the polymerization degree.

Fig. 3 represents theoretical values of ΔS^m and its constituents for a model system. One can see that in the case of $s_{12} < 0$, the concentration dependence of ΔS^m has alternating signs of its second derivative.

Fig. 4 represents the calculated concentration dependence of the partial entropy of a solvent in the solution of the glassy polymer, calculated according to:

$$\Delta S_1 = -R\left\{\ln(1 - \varphi_2) + \left(1 - \frac{1}{p}\right)\varphi_2\right\} + s_{12}\left(1 - \varphi_v^0\right)\varphi_2^{(1/\varphi_v^0)-1} \tag{11}$$

One can see that while the combinatorial entropy is a monotonously increasing positive function of concentration, ΔS_1 for the glassy polymer exhibits a minimum at high concentrations. This was observed in the experiment for the solutions of PS [18].

Combination of Eqs. (6) and (10) gives the values of Gibbs energy of mixing:

$$\Delta G^m = RT\left(x_1 \ln \varphi_1 + \frac{x_2}{p}\ln \varphi_2\right) + (\varepsilon_{22} - Ts_{12})\varphi_2\varphi_v^0\left(1 - \varphi_2^{(1/\varphi_v^0)-2}\right) \tag{12}$$

Since ε_{22} and s_{12} both are negative, there is a compensation of these terms, the glassy-state contribution to ΔG^m is less

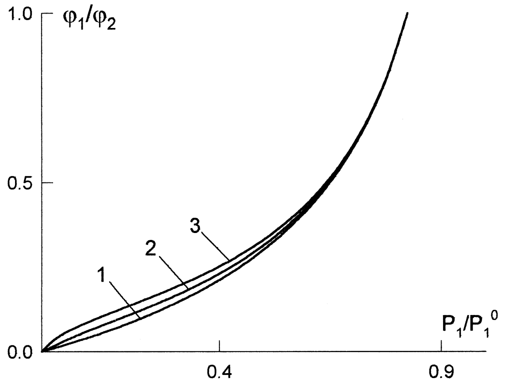

Fig. 5. Calculated vapor sorption isotherms ($\chi = 0$) for the model solution of elastomer (1) and polymer glass; $\varphi_v^0 = 0.1$, $\varepsilon_{22} = -8$ kJ/mol, $s_{12} = -10$ (2), -20 (3) J/mol K, $T = 298$ K.

than combinatorial term, and ΔG^m for the solutions of polymer glasses are close to that for the solutions of elastic polymers. Combination of Eqs. (8) and (11) reveals the chemical potential of a solvent in the solution:

$$\Delta\mu_{1,\mathrm{comb}} = RT\left\{(1-\varphi_2) + \left(1-\frac{1}{p}\right)\varphi_2\right\} + (\varepsilon_{22} - Ts_{12})\left(1-\varphi_v^0\right)\varphi_2^{(1/\varphi_v^0)-1} \quad (13)$$

One may use it to evaluate sorption isotherm of polymer glass by means of equation:

$$\Delta\mu_1 = \frac{RT}{M_1}\ln\frac{P_1}{P_1^0} \quad (14)$$

Fig. 5 represents the calculated sorption isotherms for the model glassy and elastic polymer. One can notice only minor differences between them. While the isotherm for the elastic polymer is caved downwards at any relative vapor pressure, the isotherms for glassy polymer are caved upwards at low vapor pressures which is in agreement with experimental data [17,18]. In a whole, due to the enthalpy/entropy compensation sorption isotherms are much less sensitive to the glassy nature of the polymer than enthalpy and entropy values.

3. Experimental

The enthalpy of mixing of polymers with solvents cannot be measured directly in the entire concentration range due to kinetic limitations. Therefore, the following thermochemical cycle is used [18]:

Polymer + solvent = solution of concentration ω_2 + ΔH^m
Polymer + excess of solvent = infinitely dilute solution + $\Delta H_{\mathrm{dissol}}$
Solution of concentration ω_2 + excess of solvent = infinitely dilute solution + ΔH_{dil}

The enthalpy of mixing ΔH^m is calculated according to the equation:

$$\Delta H^m = \omega_2(\Delta H_{\mathrm{dissol}} - \Delta H_{\mathrm{dil}}) \quad (15)$$

All calorimetric measurements were carried out using commercial isothermal Calvet microcalorimeters: DAK-1-1 (Chernogolovka) with 10 ml cells and sensitivity 10^{-6} J/s and MID-200 (Ethalon, Almaty) with 100 ml cells and sensitivity 5×10^{-6} J/s. The values of heat effects from 0.05 to 0.5 J were measured with ca. 5% accuracy, the values of heat effects 0.5–5 J with ca. 2%.

Samples of dry polymers and polymer solutions of definite concentration for the measurements were placed in special thin glass vessels ca. 0.5 cm^3 in volume. The amount of polymer did not exceed 30 mg by weight. Solutions of low concentration were prepared by adding the necessary amount of solvent directly into the vessel. Highly concentrated solutions were obtained by vapor sorption of solvent on polymer. The vessels were sealed and stored for several weeks to reach equilibrium. During the calorimetric experiment the vessel was broken in the calorimetric cell which contained ca. 7 cm^3 of a solvent and the heat effect was measured. The final concentration of the solution was about 0.3%.

Gibbs energy of mixing of polymer with solvent was determined by isothermal interval vapor sorption [18]. The amount of the solvent vapor adsorbed by a polymer sample at definite relative vapor pressure P_1/P_1^0 and constant temperature was measured by quartz helix microbalance with sensitivity 0.2–0.5 mg/mm in the high vacuum apparatus providing 10^{-4} mm Hg of residual pressure. The obtained vapor sorption isotherms further were treated in the usual way [18]. The change in chemical potential of the solvent upon sorption $\Delta\mu_1$ was determined according to Eq. (14). The change in chemical potential of polymer $\Delta\mu_2$ was calculated by means of Gibbs–Duhem equation:

$$\Delta\mu_2 = -\int_{-\infty}^{\Delta\mu_1} \frac{\omega_1}{\omega_2}\,\mathrm{d}\Delta\mu_1 \quad (16)$$

Using these values, Gibbs energy of mixing ΔG^m was determined with the average accuracy about 5%:

$$\Delta G^m = \omega_1\Delta\mu_1 + \omega_2\Delta\mu_2 \quad (17)$$

The entropy of mixing of polymer solution was calculated according to the well-known equation:

$$T\Delta S^m = \Delta H^m - \Delta G^m \quad (18)$$

4. Results and discussion

The parametric model described earlier was applied to fit the experimental thermodynamic functions of mixing of solutions of different glassy polymers: PS, PMMA, polyvinylacetate (PVAc), polyvinylchloride (PVC), polyacrylic acid (PAA) and some other. Calculated parameters of the model are presented in Table 1. Along with ε_{22}, s_{12},

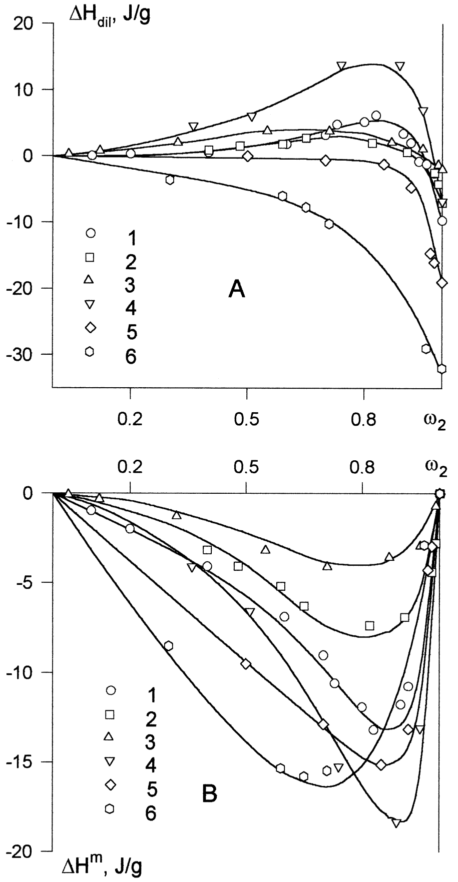

Fig. 6. Concentration dependence of the enthalpy of dilution (A) and the enthalpy of mixing (B) for PS in cyclohexane at 306 K (1), in decalene at 308 K (2), polyvinylacetate in CCl_4 at 300 K (3), poly-1-vinylpyrazole in toluene at 307 K (4), PS in ethylbenzene at 298 K (5), in chloroform at 298 K (6). Points, experimental data; solid lines, interpolation using Eqs. (22) and (23).

and φ_v^0 which describe the influence of the glassy nature of the polymer at given temperature, energetic parameters of interaction between components are also tabulated. For the enthalpy of interaction we took either Redlich–Kister expansion (19) or UNIQUAC-type expression (20) [25]. In both cases following the usual convention for polymer solutions we used volume fractions to express concentration.

$$\Delta H_{\mathrm{int}} = \varphi_1\varphi_2(A_0 + A_1(\varphi_1 - \varphi_2) + A_2(\varphi_1 - \varphi_2)^2 + \cdots)(x_1r_1 + x_2r_2) \tag{19}$$

$$\Delta H_{\mathrm{int}} = \varphi_1\varphi_2\left[\frac{C_{21}\tau_{21}}{\varphi_1 + \varphi_2\tau_{21}} + \frac{C_{12}\tau_{12}}{\varphi_2 + \varphi_1\tau_{12}}\right](x_1r_1 + x_2r_2),$$
$$\tau_{ij} = \exp\left(-\frac{C_{ij}}{RT}\right) \tag{20}$$

It is useful to pay attention to the presence of $(x_1r_1 + x_2r_2)$ multiplier in expressions (19) and (20), where r_1 and r_2 are Van der Waals volumes of components, calculated according to Bondi tables [25]. If we express the concentration in volume fractions, ΔH_{int} is, in fact, related to the unit volume of the solution. However, in practical applications it is more common to relate the thermodynamic functions of mixing to 1 mol (or 1 g) of the solution. Hence, we should multiply the corresponding expressions by the molar volume of the solution $(x_1r_1 + x_2r_2)$. Note that this should be applied to the expressions (6) and (9) for ΔH_g and ΔS_g but not to combinatorial entropy which is related to 1 mol of solution by definition.

Thus, all the energetic constants in Table 1, obtained by fitting experimental data, are related to the unit volume.

If necessary, one can easily estimate Flory–Huggins parameter of interaction per unit volume from tabulated energetic parameters using the following relations:

$$\chi = \frac{A_0}{RT}\ (A_1, A_2, \ldots = 0), \qquad \chi = \frac{C_{12} + C_{21}}{RT}$$

In all cases correlation of interpolated dependence and experimental data exceeded 98% level which is in the limits of experimental error for ΔH^m, ΔG^m, and ΔS^m values.

The general validity of theoretical approach will be illustrated by two examples.

4.1. The enthalpy of mixing in the solutions with UCST

Fig. 6(a) represents the experimental values of ΔH_{dil} (points) for several solutions of glassy polymers. Plots 1–4 correspond to the systems where the phase separation upon cooling takes place: PS–cyclohexane (UCST = 306 K), PS–decalene (UCST = 279 K), PVAc–CCl_4 (UCST = 300 K), poly-1-vinylpyrazole–toluene (UCST = 307 K) [26]. Calorimetric measurements were performed in homogeneous solutions above UCST. In these four systems the enthalpy of dilution is positive in almost entire concentration range except in the very concentrated solutions and the pure polymer itself, where it is negative. Such character of concentration dependence stems from the superposition of poor interaction of components (endothermic contribution) and the relaxation of metastable structure of glass (exothermic contribution). Due to the negative sign of the enthalpy of dissolution (which is, in fact, ΔH_{dil} at $\omega_2 = 1$) the values of ΔH^m calculated according to Eq. (15) are negative over the entire concentration range. They are presented in Fig. 6(b).

One can notice that the concentration dependence of ΔH^m for the solutions of polymer glasses with UCST has different curvature in dilute and concentrated regions. This is an important feature. According to Prigogine and Defay [27], the sign of the second derivative of the dependence of enthalpy (and entropy) of mixing at the critical concentration is the necessary thermodynamic condition for the

Table 1
Parameters of the model for the solutions of some glassy polymers

System	T (K)	r_2	r_1	M	A_0 (J/mol)	A_1 (J/mol)	A_2 (J/mol)	C_{21} (J/mol)	C_{12} (J/mol)	ε_{22} (J/mol)	s_{12} (J/mol K)	φ_v^0
PS–benzene	298	4.14	3.1878	6.8×10^5	0	–	–	0	0	−8200	−34.0	0.06
PS–toluene	298	4.14	3.9228	6.8×10^5	0	–	–	0	0	−8100	−32.9	0.07
PS–ethylbenzene	298	4.14	4.5972	6.8×10^5	0	–	–	0	0	−8170	−29.3	0.06
PS–decalene	308	4.14	6.2890	2×10^5	74	–	–	1	73	−5020		0.05
PS–cyclohexane	306	4.14	4.05	1×10^6	619.5	−354	88.5	–	–	−7890	−25.0	0.08
PS–cyclohexene	298	4.14	3.8179	6.8×10^5	420	−240	60	–	–	−7100	−24.0	0.10
PS–chloroform	298	4.14	2.87	6.8×10^5	−220	–	–	−110	−110	−8010	−28.1	0.08
PMMA–chloroform	298	3.6981	2.87	5×10^5	−1075	–	–	−545	−530	−14 190	−54.4	0.11
PMMA–ethylacetate	298	3.6981	3.4786	5×10^5	−30	–	–	−15	−15	−11 410	−50.0	0.08
PMMA–DMFA	298	3.6981	3.0856	5×10^5	306	−181	–	–	–	−11 050		0.07
PVAc–CCl_4	300	3.2519	3.39	3×10^5	155	–	–	77	78	−2140	−8.0	0.09
PVAc–toluene	298	3.2519	3.9228	3×10^5	151	−86	22	–	–	−1630	−7.5	0.09
PVAc–dichloroethane	298	3.2519	2.9308	3×10^5	−31	–	–	−15	−16	−2060	−8.4	0.09
PVC–THF	298	1.9124	2.9415	7×10^4	−264	–	–	−132	−132	−9160	−47.7	0.09
PVC–cyclohexanone	298	1.9124	4.1433	7×10^4	−306	–	–	−153	−153	−4150		0.13
PVC–dimethylphtalate[a]	298	1.9124	6.6618	7×10^4	210	–	–	105	105	−5300		0.12
PVC–diethylphtalate[a]	298	1.9124	8.0106	7×10^4	8	–	–	8	0	−5300		0.11
PVC–dibutylphtalate[a]	298	1.9124	10.708	7×10^4	−150	–	–	−75	−75	−4200	−30.2	0.12
PVC–dioctylphtalate[a]	298	1.9124	16.102	7×10^4	−353	–	–	−175	−178	−4070		0.13
PVC–dinonylphtalate[a]	298	1.9124	17.448	7×10^4	−434	–	–	−217	−217	−3900		0.13
PVC–didodecylphtalate[a]	298	1.9124	21.499	7×10^4	−510	–	–	−255	−255	−3700		0.13
PVC–ditridecylphtalate[a]	298	1.9124	22.847	7×10^4	−708	–	–	−354	−354	−3160		0.11
PAA–DMFA	298	2.6501	3.0856	1.2×10^5	−2406	802	–	–	–	−25 580		0.20
	305	2.6501	3.0856	1.2×10^5	−6102	2034	–	–	–	−11 000		0.20
PAA–butanole	298	2.6501	3.9243	1.2×10^5	176	–	–	88	88	−14 480		0.13
	305	2.6501	3.9243	1.2×10^5	232	–	–	166	166	−10 430		0.13
Poly-1-vinylpyrazole–toluene	307	3.4232	3.9228	2×10^4	1157	−386	–	–	–	−12 710		0.08
Poly-1-vinylpyrazole–DMFA	298	3.4232	3.0856	2×10^4	−318	–	–	−159	−159	−3950		0.09
Poly-1-vinylimidazole–DMFA	298	3.4232	3.0856	2×10^4	68	–	–	34	34	−9960		0.14

[a] Experimental values of thermodynamic functions of mixing were determined using thermodynamic cycle which included dissolution of components and their composition in the excess of a common solvent [18].

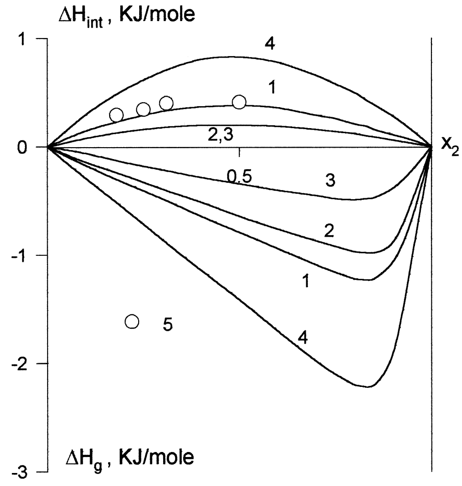

Fig. 7. The calculated interaction and glassy-state contributions to the enthalpy of mixing for PS in cyclohexane at 306 K (1), PS in decalene at 308 K (2), polyvinylacetate in CCl_4 at 300 K (3), poly-1-vinylpyrazole in toluene at 307 K (4). The enthalpy of mixing of ethylbenzene with cyclohexane at 298 K [28] (5).

existence of liquid–liquid phase separation in the system:

$$\text{UCST}: \quad \frac{\partial^2 \Delta H^{\mathrm{m}}}{\partial \omega_2^2} < 0 \qquad \text{LCST}: \quad \frac{\partial^2 \Delta H^{\mathrm{m}}}{\partial \omega_2^2} > 0 \tag{21}$$

The critical concentration $\omega_{2,\mathrm{cr}}$ in polymer solutions is low and hence the curves 1–4 presented in Fig. 6(b) obey the thermodynamic criterion (21).

According to Eq. (1), the experimental values of ΔH^{m} consists of two contributions, and the proposed theory can estimate them separately. The parameters of the theory for the solutions with UCST were calculated by interpolating the experimental data on ΔH_{dil} using the combination of Eqs. (7), (15), (19) and (20). For the enthalpy of dilution per mole of monomer units it gives:

$$\Delta H_{\mathrm{dil}} = A_0\varphi_2 + A_1\left(3\varphi_2 - 2\varphi_2^2\right) + A_1\left(5\varphi_2 - 8\varphi_2^2 + 4\varphi_2^3\right) + \varepsilon_{22}\varphi_{\mathrm{v}}^0\varphi_2^{(1/\varphi_{\mathrm{v}}^0)-2} \tag{22}$$

$$\Delta H_{\mathrm{dil}} = C_{12} + C_{21}\tau_{21} - \varphi_1\left(\frac{C_{21}\tau_{21}}{\varphi_1 + \varphi_2\tau_{21}} + \frac{C_{12}\tau_{12}}{\varphi_2 + \varphi_1\tau_{12}}\right) + \varepsilon_{22}\varphi_{\mathrm{v}}^0\varphi_2^{(1/\varphi_{\mathrm{v}}^0)-2} \tag{23}$$

The result of interpolation is presented by solid lines in Fig. 6(a) and (b). The estimated parameters are given in Table 1. Although these are the adjustable parameters, their values are reasonable. They were used for the calculation of ΔH_{int} and ΔH_{g} terms according to the expressions (19), (20) and (6), respectively.

The concentration dependence of the calculated values of ΔH_{int} and ΔH_{g} is presented in Fig. 7. The values of ΔH_{int} are positive over the entire concentration range which means that intermolecular interactions in the solutions are poor. This is the basic reason for the phase separation in these systems. Meanwhile, the values of ΔH_{g} are negative over the entire concentration range and provide the negative sign of the integral values of ΔH^{m}. The values of ΔH_{int} for the solution of PS in cyclohexane are compared with the experimental data [28] for the system cyclohexane–ethylbenzene (hydrogenated monomer of PS). The close correlation between them confirms the validity of the approach.

4.2. Gibbs energy and the entropy of mixing of polystyrene solutions

Fig. 8(a) represents the vapor sorption isotherms for the solutions of PS in chloroform (a good solvent), ethylbenzene (monomer analog), and cyclohexane (a poor solvent). All isotherms have typical shape for the polymer solutions, and they are slightly curved upwards at low relative pressure of the solvent vapor. The sorption of chloroform and ethylbenzene on PS is almost the same within the experimental error, while the sorption of cyclohexane is much lower.

The experimental data were used for the calculation of Gibbs energy of mixing of the solutions of PS according to expressions (14), (16) and (17). The experimental concentration dependence of ΔG^{m} is presented in Fig. 8(b). The values of ΔG^{m} are negative for all systems over the entire concentration range, and the second derivative of ΔG^{m} is positive. This means that the solutions are thermodynamically compatible and homogeneous. For chloroform and ethylbenzene solutions the values of ΔG^{m} are close to each other and to the combinatorial Gibbs energy of mixing which is presented by the dashed line. The values of ΔG^{m} for PS solution in cyclohexane are less negative owing to the nearby phase separation of the system.

The enthalpy of mixing of PS with cyclohexane was discussed in Section 4.1. As for the solutions in chloroform and ethylbenzene, the values of ΔH^{m} were determined according to Eq. (15) using the experimental values of ΔH_{dil} presented in Fig. 6(a) (curves 5 and 6). The concentration dependence of ΔH_{dil} is different from that for the solutions with UCST. In the case of ethylbenzene ΔH_{dil} is close to zero in a wide concentration range and large and negative in concentrated solutions. The whole curve looks very much like the ΔH_{dil} plot for the model polymer glass in the athermal solvent (Fig. 2) which is quite reasonable. In the case of chloroform ΔH_{dil} is negative over the entire concentration range.

The values of ΔH^{m} for the solutions of PS in chloroform and ethylbenzene calculated according to Eq. (15) are presented in Fig. 6(b) (curves 5 and 6). They are negative over the entire concentration range. The concentration dependence of ΔH^{m} has positive second derivative. The experimental data were theoretically interpolated and the estimated values of parameters are presented in Table 1.

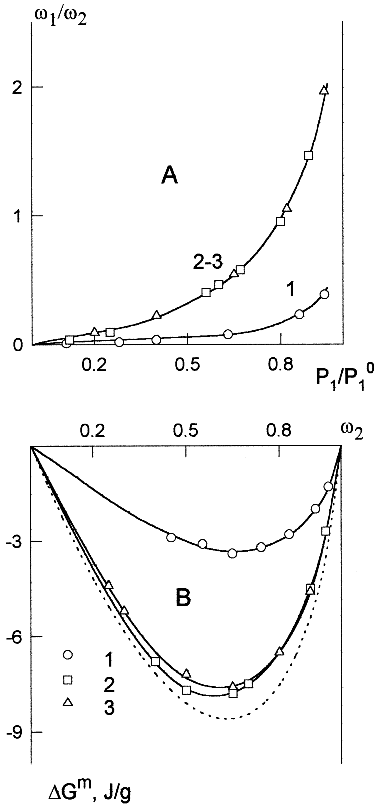

Fig. 8. Experimental vapor sorption isotherms (A) and Gibbs energy of mixing (B) for PS in cyclohexane at 306 K (1), ethylbenzene at 298 K (2), and in chloroform at 298 K (3). Dashed line, combinatorial values.

The values of ΔG^{m} and ΔH^{m} were used for the determination of the entropy of mixing in the solutions of PS according to Eq. (18). The values of $T\Delta S^{\mathrm{m}}$ are presented in Fig. 9. For all the systems $T\Delta S^{\mathrm{m}}$ is large and negative, and the second derivative of its concentration dependence has different signs just like for the model system in Fig. 3. Since in any solution there is the large positive combinatorial entropy of mixing, one would expect strong negative contribution of the glassy nature of PS. The values of $T\Delta S^{\mathrm{m}}$ were interpolated using Eq. (10). The estimated values of parameter φ_{v}^{0} were very close to that determined from ΔH^{m} data, the values of adjustable parameter s_{12} are given in Table 1. The latter are negative for all the systems. The same negative sign of s_{12} was obtained for all the solutions of glassy polymers studied up to date. Basically that is the reason of calling it the entropy depression parameter. However, since s_{12} is the superposition, probably there might exist solutions with the positive sign of it.

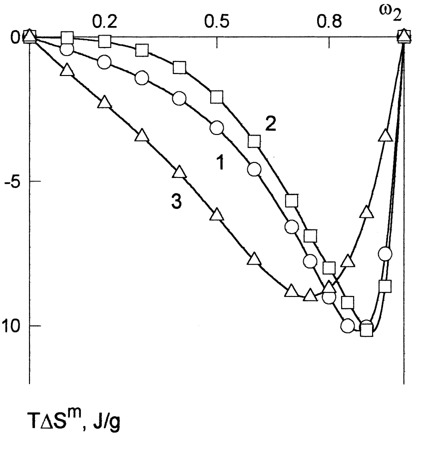

Fig. 9. The experimental values of the entropy of mixing for PS in cyclohexane at 306 K (1), ethylbenzene at 298 K (2), and in chloroform at 298 K (3).

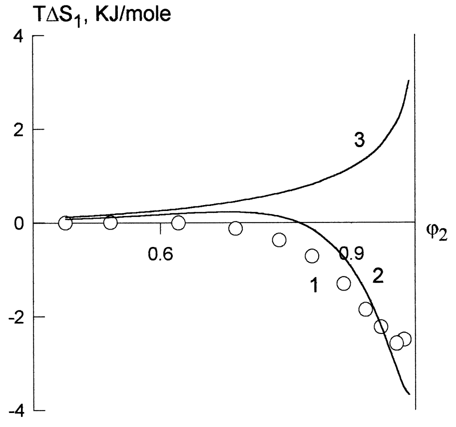

Fig. 10. The excess partial entropy of chloroform in PS solution at 298 K. (1) Experimental values; (2) calculated according to Eq. (11), using parameters of Table 1; (3) combinatorial term ($s_{12} = 0$).

The experimental and interpolated values of $T\Delta S^{\mathrm{m}}$ together with its constituents are presented in Table 2 for the solutions with $\omega_2 = 0.5$. The values of $T\Delta S_{\mathrm{g}}$ are negative and dominate over positive values of $T\Delta S_{\mathrm{comb}}$. This makes integral values of $T\Delta S^{\mathrm{m}}$ for the solutions of glassy polymers also negative.

Negative contribution to the entropy shows not only in the values of $T\Delta S^{\mathrm{m}}$ but also in the partial quantities as well. Fig. 10 presents the concentration dependence of the excess partial entropy of chloroform in the solution of PS. Experimental points are obtained by the combination of experimental values of $\Delta\mu_1$ determined from the sorption isotherm according to Eq. (14) and the values of ΔH_1 calculated from the concentration dependence of ΔH^{m} using the well-known approach [25]. The solid line corresponds to the predicted values calculated according to the expression (11). The experimental data are in satisfactory agreement with the semi-empirical model.

Although the enthalpy and entropy of mixing of PS solutions strongly depend on the glassy nature of the polymer, Gibbs energy values are, on the contrary, rather insensitive to that influence. This might be clearly seen from Fig. 8(b), where the values of ΔG^{m} for the good solvent (chloroform) are not only close to the values for the monomer analog (ethylbenzene) but as well to the combinatorial Gibbs energy of mixing (dashed line). This is the result of the superposition of negative contribution of the glassy

Table 2
Entropy of mixing and its constituents for PS solution at $\omega_2 = 0.5$

System	$T\Delta S_{\mathrm{comb}}$ (J/g)	$T\Delta S_{\mathrm{g}}$ (J/g)	$T\Delta S^{\mathrm{m}}_{\mathrm{calc}}$ (J/g)	$T\Delta S^{\mathrm{m}}_{\mathrm{exp}}$ (J/g)
PS–cyclohexane, 306 K	8.8	−11.8	−3.0	−3.1
PS–ethylbenzene, 298 K	8.0	−10.0	−2.0	−2.1
PS–chloroform, 298 K	8.2	−12.3	−4.2	−6.1

structure to the enthalpy and entropy of mixing usually referred to as enthalpy/entropy compensation.

4.3. General remarks on the other systems in Table 1

Parameters of interaction $A_0, A_1, A_2, C_{21}, C_{12}$, presented in Table 1, depend on the nature of the certain components of solution and we would not discuss them here, but focus on the parameters ε_{22}, s_{12}, and φ_{v}^{0} which describe the influence of the glassy nature of the polymer. Since they are adjustable, we would not put too much importance on the certain values of them. However, some preliminary assumptions still can be made.

For all the polymers the values of the volume fraction of metastable voids (φ_{v}^{0}) are rather low which is quite reasonable. The values of cohesion energy (ε_{22}) are large and negative. For all the systems they provide negative integral values of ΔH^{m} over the entire concentration range except the solution of PVAc in toluene in which ΔH^{m} has alternating signs. For PS the average value of ε_{22} per unit volume is 7910 J/mol, which yields 32.8 kJ/mol per monomer unit. This is surprisingly close to the increment evaluation of cohesion energy of PS: 32.5 kJ/mol [18,29]. The values of ε_{22} correctly reflect the influence of polarity, thus for PMMA they are more negative due to stronger interactions between polar groups. The lowest values of ε_{22} were found for PVAc solutions. Most likely this is because at ambient conditions this polymer is very close to its glass transition ($T_{\mathrm{g}} = 315$ K [8]).

While in the case of PS, PMMA, PVAc, the values of ε_{22} do not differ much for the different solutions, it is not so for the other polymers. In fact, taking into account the simplicity of the model and the effective integral character of ε_{22}, we would rather be surprised by the relatively uniform values of ε_{22} for PS than the dispersion of it, for instance, in the case of PVC. In general, the values of ε_{22} appear to be more sensitive to the nature of the system and the temperature than the values of φ_{v}^{0}. This can hardly be explained in the framework of the presented approach and needs more solid theoretical grounds for the discussion.

The entropy depression parameter s_{12} is negative for all the systems and correlates with the cohesion energy ε_{22}. In the solutions of PS, PMMA, PVC the glassy-state contribution dominates over the combinatorial term in ΔS^{m}, and the integral values of the entropy of mixing are negative. However, in the solutions of PVAc the absolute values of s_{12} are lower and the integral entropy of mixing is positive.

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