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Determination of pair interaction parameters for multicomponent polymer blends

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Pair interaction parameters for multicomponent polymer blends were found to be determined by analyzing the sorption isotherms of common solvent.

Key words: thermodynamics, polymer blends, pair interaction parameters, free energy of mixing, sorption isotherms.

The necessity of obtaining information on thermodynamic characteristics of polymer blends does not admit of doubt. Among a variety of characteristics, there are pair interaction parameters (Huggins parameters).[1—3] When these parameters are available, it is possible to establish how the free energy of mixing depends on the polymer blend composition, to evaluate the mutual solubility limits of the blend components, and to construct the phase diagrams and various sections of these diagrams.

Our experience on studies of the phase equilibria in the polymer—polymer systems suggests that it is of crucial importance to obtain information on the pair interaction parameters (χ_{ij}) by processing experimental data using independent procedures. Clearly, this can be useful for not only solving problems mentioned above but also testing correctness of statistical theories of polymer melts and solutions.

The aim of this work was to determine the pair interaction parameters between the components of multicomponent polymer blends by analyzing the sorption isotherms of common solvent.

According to the Flory—Huggins theory of polymer solutions,[4—7] the expression for the free energy of mixing (ΔG_m) of an n-component system has the form

$$\frac{\Delta G_m}{RT} = \sum_{i=1}^{n} \frac{\varphi_i \ln \varphi_i}{r_i} + \sum_{i=1}^{n-1} \varphi_i \left(\sum_{j=i+1}^{n} \chi_{ij} \varphi_j \right), \qquad (1)$$

where φ_i and φ_j are respectively the concentrations of the ith and jth components in solution (blend) expressed in the volume fraction scale, r_i is the degree of polymerization of the ith component, and n is the total number of components in the system. The component concentrations are related by obvious relationship

$$\sum_{i=1}^{n} \varphi_i = 1.$$

A specific feature of the system under study is that the ratio of the polymer concentrations in the blend is the same in all portions of sorption isotherms. This allows such systems to be treated as pseudobinary "sorbate—sorbent" systems characterized by the solvent concentration (φ_S) and the polymeric sorbent concentration φ_P ($\varphi_S + \varphi_P = 1$). Clearly, the polymer concentrations in the sorbent in all portions of sorption isotherms are given by

$$\varphi_i = \varphi_P k_i, \qquad (2)$$

where k_i is the concentration of the ith polymer in the blend in the absence of solvent.

Consider the thermodynamics of mixing of a pseudobinary system assuming constant values of the pair interaction parameters at all concentrations.

By substituting expression (2) in expression (1), grouping similar terms, and denoting the degree of polymerization of the polymeric sorbent (r_P) as

$$\frac{1}{r_P} = \sum_{i=1}^{m} \frac{k_i}{r_i},$$

we get

$$\frac{\Delta G_m}{RT} = \frac{\varphi_P \ln \varphi_P}{r_P} + \varphi_S \ln \varphi_S + \varphi_P \sum_{i=1}^{m} \frac{k_i \ln k_i}{r_i} + \varphi_P^2 \sum_{i=1}^{m-1} k_i \left(\sum_{j=i+1}^{m} \chi_{ij} k_j \right) + \varphi_P \varphi_S \sum_{i=1}^{m} \chi_{iS} k_i, \qquad (3)$$

where m is the number of polymeric components in the sorbent. The third and fourth terms represent the entropy-dependent part of the free energy of mixing of polymers ($\Delta G_{m,P}$) in the absence of solvent

$$\frac{\Delta G_{m,P}}{RT} = \sum_{i=1}^{m} \frac{k_i \ln k_i}{r_i} + \sum_{i=1}^{m-1} k_i \left(\sum_{j=i+1}^{m} \chi_{ij} k_j \right). \qquad (4)$$

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By transforming expression (4)

$$\sum_{i=1}^{m}\frac{k_i\ln k_i}{r_i}=\frac{\Delta G_{\mathrm{m,P}}}{RT}-\sum_{i=1}^{m-1}k_i\left(\sum_{j=i+1}^{m}\chi_{ij}k_j\right)$$

and substituting it into Eq. (3), one has

$$\frac{\Delta G_{\mathrm{m}}}{RT}=\frac{\varphi_{\mathrm{P}}\ln\varphi_{\mathrm{P}}}{r_{\mathrm{P}}}+\varphi_{\mathrm{S}}\ln\varphi_{\mathrm{S}}+\varphi_{\mathrm{P}}\frac{\Delta G_{\mathrm{m,P}}}{RT}-$$

$$-\varphi_{\mathrm{P}}\sum_{i=1}^{m-1}k_i\left(\sum_{j=i+1}^{m}\chi_{ij}k_j\right)+\varphi_{\mathrm{P}}^2\sum_{i=1}^{m-1}k_i\left(\sum_{j=i+1}^{m}\chi_{ij}k_j\right)+\varphi_{\mathrm{P}}\varphi_{\mathrm{S}}\sum_{i=1}^{m}\chi_{i\mathrm{S}}k_i$$

or, after transformation,

$$\frac{\Delta G_{\mathrm{m}}}{RT}=\frac{\varphi_{\mathrm{P}}\ln\varphi_{\mathrm{P}}}{r_{\mathrm{P}}}+\varphi_{\mathrm{S}}\ln\varphi_{\mathrm{S}}+\varphi_{\mathrm{P}}\frac{\Delta G_{\mathrm{m,P}}}{RT}+$$

$$+\left[\sum_{i=1}^{m}\chi_{i\mathrm{S}}k_i-\sum_{i=1}^{m-1}k_i\left(\sum_{j=i+1}^{m}\chi_{ij}k_j\right)\right]\varphi_{\mathrm{P}}\varphi_{\mathrm{S}}.$$

Finally, by denoting

$$\chi_{\mathrm{PS}}=\sum_{i=1}^{m}\chi_{i\mathrm{S}}k_i-\sum_{i=1}^{m-1}k_i\left(\sum_{j=i+1}^{m}\chi_{ij}k_j\right), \tag{5}$$

one gets

$$\frac{\Delta G_{\mathrm{m}}}{RT}=\frac{\varphi_{\mathrm{P}}\ln\varphi_{\mathrm{P}}}{r_{\mathrm{P}}}+\varphi_{\mathrm{S}}\ln\varphi_{\mathrm{S}}+\chi_{\mathrm{PS}}\varphi_{\mathrm{P}}\varphi_{\mathrm{S}}+\varphi_{\mathrm{P}}\frac{\Delta G_{\mathrm{m,P}}}{RT}. \tag{6}$$

From Eq. (6) it follows that, for obvious reasons, for the polymer—solvent system one has $\Delta G_{\mathrm{m,P}} = 0$ and this equation is reduced to conventional equation for the free energy of mixing of a binary system.

The degree of polymerization of a binary polymeric sorbent is defined by

$$1/r_{\mathrm{P}} = k_1/r_1 + k_2/r_2,$$

and the effective parameter of the sorbent—solvent pair interaction (see Eq. (5)) is given by

$$\chi_{\mathrm{PS}} = \chi_{1\mathrm{S}}k_1 + \chi_{2\mathrm{S}}k_2 - \chi_{12}k_1k_2.$$

For a ternary sorbent, one has

$$1/r_{\mathrm{P}} = k_1/r_1 + k_2/r_2 + k_3/r_3,$$

and

$$\chi_{\mathrm{PS}} = \chi_{1\mathrm{S}}k_1 + \chi_{2\mathrm{S}}k_2 + \chi_{3\mathrm{S}}k_3 - \chi_{12}k_1k_2 - \chi_{13}k_1k_3 - \chi_{23}k_2k_3 \tag{7}$$

respectively.

Noteworthy is that Eq. (6) differs from the equation for the binary system by the term proportional to the free energy of mixing of polymers and that the right side of Eq. (6) differs from zero at $\varphi_{\mathrm{P}} = 1$.

Using Eq. (6), it is possible to derive expressions for the chemical potentials of the solvent (sorbate, $\Delta\mu_{\mathrm{S}}$) and the polymer blend (sorbent, $\Delta\mu_{\mathrm{P}}$)

$$\Delta\mu_{\mathrm{S}}/RT = \ln\varphi_{\mathrm{S}} + (1 - 1/r_{\mathrm{P}})\varphi_{\mathrm{P}} + \chi_{\mathrm{PS}}\varphi_{\mathrm{P}}^2, \tag{8}$$

$$\Delta\mu_{\mathrm{P}}/RT = (\ln\varphi_{\mathrm{P}})/r_{\mathrm{P}} + (1/r_{\mathrm{P}} - 1)\varphi_{\mathrm{S}} + \chi_{\mathrm{PS}}\varphi_{\mathrm{S}}^2 + \Delta G_{\mathrm{m,P}}/RT.$$

The sorption isotherm relates the chemical potential of the solvent ($\Delta\mu_{\mathrm{S}}$) and the equilibrium solvent concentration in the sorbent (φ_{S}). Because of this, the free energy of mixing (see expression (6)) can be calculated using the Gibbs—Duhem equation for a binary system in the form

$$\Delta\mu_{\mathrm{P}} = -\int_{-\infty}^{\Delta\mu_{\mathrm{S}}}\frac{\varphi_{\mathrm{S}}}{\varphi_{\mathrm{P}}}\partial(\Delta\mu_{\mathrm{S}})$$

or

$$\Delta\mu_{\mathrm{P}} = -RT\int_{0}^{p/p_0}\frac{\varphi_{\mathrm{S}}}{\varphi_{\mathrm{P}}\left(\frac{p}{p_0}\right)}\partial\left(\frac{p}{p_0}\right).$$

Thus, the pair interaction parameters can be determined either by analyzing the sorption isotherms using Eq. (8) or from Eq. (6) using the known values of the free energy of mixing.

Treatment of the sorption isotherms gives a set of parameters χ_{PS} that depend on the component ratio in the polymeric sorbent. To determine all the pair interaction parameters χ_{ij} for the *n*-component system from Eq. (5) using the χ_{PS} data set, one should have at least $\sum_{i=1}^{n-1} i$ sorption isotherms obtained at different (linearly independent) concentrations of the polymeric components. For instance, at least three sorption isotherms are required for a binary polymeric sorbent, at least six sorption isotherms are needed for a three-component polymeric sorbent, *etc.*

To evaluate this procedure for calculations of the pair interaction parameters for multicomponent systems, we used seven isotherms of water vapor sorption by polyvinylpyrrolidone (PVP)—poly(ethylene glycol) (PEG) blends with different compositions and eight isotherms of water vapor sorption by PVP—PEG—poly(acrylic acid) (PAA) blends.

Typical sorption isotherms are shown in Figs 1 and 2. In all cases we dealt with the equilibrium sorption isotherms that were reproducible in the sorption—desorption cycles. This is a necessary condition for obtaining correct information on the pair interaction parameters from experimental data.

The experimental data were processed as follows. Using Eq. (8) and the sorption isotherms of particular polymeric sorbents (blends), we determined the effective parameters of the corresponding pair interaction between the polymeric sorbent and the sorbate (χ_{PS}). The Huggins

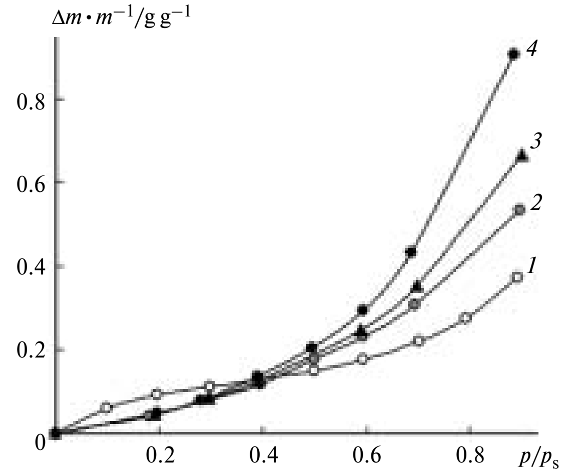

Fig. 1. Isotherms of water vapor sorption by PVP—PEG blends with different compositions: PVP (*1*), PVP—PEG (25 wt.%) (*2*), PVP—PEG (33 wt.%) (*3*), and PVP—PEG (50 wt.%) (*4*); Δm is the increase in the weight of the sample, m is the weight of the initial sample, and p_s is the saturated vapor pressure.

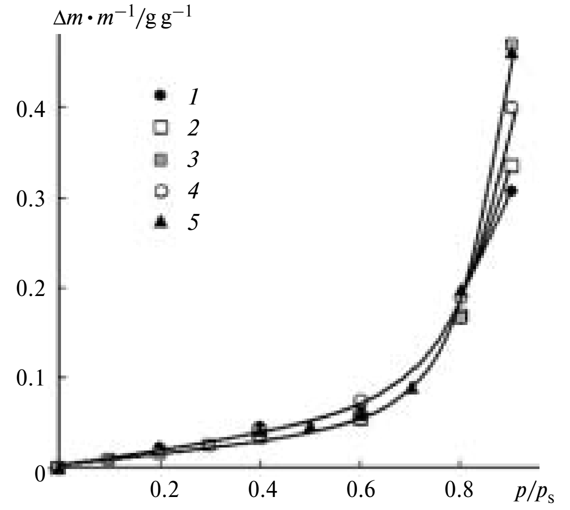

Fig. 2. Isotherms of water vapor sorption by PVP—PEG—PAA blends (sorbents) with different compositions (wt.%): 70.8 : 15.0 : 14.2 (*1*), 58 : 30 : 12 (*2*), 50 : 40 : 10 (*3*), 41.7 : 50.0 : 8.3 (*4*), and 70 : 15 : 15 (*5*). For Δm, m and p_s, see Caption to Fig. 1.

parameters thus obtained and the pair interaction parameters for two binary systems, PVP—water and PEG—water,[8,9] are listed in Table 1. The calculated values of the pair interaction parameters are in good agreement with one another. Large negative values of the Huggins parameters characterizing the interactions between PAA and other components are probably due to specific interactions between functional groups of the PVP, PAA, and PEG molecules.[10]

Thus, the pair interaction parameters for components of multicomponent polymer blends can be determined by analyzing the sorption isotherms of common solvent.

Table 1. Pair interaction parameters (χ_{ij}) for polymer blends (sorbents)

Interacting pair	χ_{ij}		
	PVP—PEG—PAA	PVP—PEG	Homopolymers
PVP—water	0.84	0.65	0.6—1.1
PAA—water	0.08	—	—
PEG—water	0.4	0.38	0.4
PVP—PAA	−1.81	—	—
PVP—PEG	−0.23	−0.24	—
PAA—PEG	−7.37	—	—

Experimental

Sorption isotherms were obtained using static sorption technique on a McBain sorption balance following a known procedure[11] at 25 °C. The pair interaction parameters were determined using Eq. (7) by the least squares method with an accuracy of 15%.

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