Thermodynamics of Mixing Polymethylene and Polyisobutylene

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ABSTRACT: Thermodynamic mixing functions for this system are calculated on the basis of characteristic parameters for the respective pure components derived from their equation-of-state coefficients. The contribution from interactions between neighbors is very nearly negligible. Calculated excess functions at equal segment fraction composition are excess volume, 0.03%; $\Delta H_{\mathrm{M}} = 2.5$ cal/100 g; $T\Delta S_{\mathrm{M}} = -6$ cal/100 g; $\Delta G_{\mathrm{M}} = 8.5$ cal/100 g. Variations with temperature are insignificant from 25 to 150°. The positive free energy of mixing signifies mutual incompatibility of these polymers at equilibrium.

The formation of a solution from two polymers of high molecular weight presents a circumstance without parallel among solutions of low molecular compounds. Not only are the rates for diffusional processes very low, but the principal factor normally operative in promoting mixing is vastly diminished. We refer to the tendency of molecules, subject to thermal motions and acting as separate kinetic units, to distribute themselves throughout the available volume at random. For molecular mixtures this tendency is normally responsible for the ideal mixing terms in the expressions for the chemical potentials, and it renders the activity of each species proportional to its concentration at sufficiently low concentrations. For a mixture of two polymers the ideal terms vanish from the chemical potentials, relative to contributions from terms of higher order in the concentration, in the limit of infinite chain length for both species. The activities are no longer proportional to the respective concentrations at any finite composition. The ideal solution is not a suitable prototype for such a mixture, and conventional precepts of solubility are best abandoned. The thermodynamic mixing functions are determined entirely by nonideal, or excess, contributions. These characteristics are direct and obvious consequences of the disappearance of molecules as separate entities in the stated limit.

As we have shown in preceding papers,[1,2] the excess (or residual[3]) properties for a binary mixture depend on the characteristic parameters v^*, T^*, and p^* for each of the pure components, and also on the pair interaction parameter X_{12}.

The characteristic parameters for amorphous polymethylene (PM) have been determined by Orwoll and Flory[4] by direct measurement above 134° and at lower temperatures by extrapolation of results for *n*-alkanes. The parameters for polyisobutylene (PIB) are reported in the preceding paper.[5] We shall designate the former (PM) as component 1, and the latter (PIB) as component 2. The parameter X_{12} characterizing the exchange of neighbor interactions which accompanies mixing may be ascertained from the analysis of enthalpies of mixing PIB with various *n*-alkanes, treated in the first paper[1] of the present series. In this manner we obtain $X_{12} = 0.20 \pm 0.10$ cal cc^{-1}, a very small value. The neighbor interactions are nearly neutral with respect to exchange of species. In fact, the results which follow would be little affected by taking $X_{12} = 0$. Accordingly, they are not subject to serious error resulting from inaccuracy in the extrapolated value of X_{12}.

The required data are thus in hand for calculating the thermodynamic excess functions for mixtures of PM and PIB, both being in the liquid, or amorphous, state. These functions can only be evaluated indirectly, as by theoretical calculation, inasmuch as the high viscosities of the polymers and their mixtures preclude the conduct of experiments suitable for direct determination of changes accompanying mixing. The mutual compatibility of two polymers at equilibrium is a question of considerable interest in this connection,[6,7] and one that does not readily lend itself to resolution by a definitive experiment. The calculations which follow are illustrative of a means for circumvention of this difficulty.

Theoretical Relationships

The standard unit, namely, the gram mole, normally adopted for expression of thermodynamic functions of mixtures should obviously be replaced for the system considered. In its stead, we choose the gram. The mixing functions per gram of mixture of polymers of infinite chain length are given by[2]

$$\Delta H_{\mathrm{M}} \equiv H_{\mathrm{M}}^{\mathrm{R}} = v_{\mathrm{sp}}^*[\varphi_1 p_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \varphi_2 p_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1}) + (\varphi_1\theta_2/\tilde{v})X_{12}] \quad (1)$$

$$\Delta S_{\mathrm{M}} \equiv S_{\mathrm{M}}^{\mathrm{R}} = -3v_{\mathrm{sp}}^*\{(\varphi_1 p_1^*/T_1^*)\ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\varphi_2 p_2^*/T_2^*) \times \ln[(\tilde{v}_2^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\} \quad (2)$$

and of course

$$\Delta G_{\mathrm{M}} \equiv G_{\mathrm{M}}^{\mathrm{R}} = \Delta H_{\mathrm{M}} - T\Delta S_{\mathrm{M}} \quad (3)$$

Here $v_{\mathrm{sp}}^* = w_1 v_{\mathrm{sp};1}^* + w_2 v_{\mathrm{sp};2}^*$ is the characteristic volume for 1 g of mixture, $\tilde{v}$ is its reduced volume calcu-

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(1) P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, **1**, 279 (1968).

(2) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).

(3) Excess and residual properties may be considered to be identical if both components of the binary mixture are of sufficiently high molecular weight. This will be apparent from the mixing functions.[1,2]

(4) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **69**, 6814 (1967); R. A. Orwoll, Ph.D. Thesis, Stanford University, 1966.

(5) B. E. Eichinger and P. J. Flory, *Macromolecules*, **1**, 285 (1960).

(6) R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).

(7) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 554–555.

Table I

Characteristic Parameters for Polymethylene[a]

t, °C	v_{sp}^*, cc g^{-1}	p^*, cal cc^{-1}	T^*, °K	$\tilde{T}$	$\tilde{v}$
25	1.000	116	6500	0.0459	1.182
100	1.013	113	7010	0.0532_3	1.224_0
150	1.026	109.5	7359	0.05750	1.2510

[a] See ref 4.

Table II

Thermodynamic Mixing Functions for Polymethylene–Polyisobutylene at Equal Segment Fractions

t, °C	$\tilde{v}$	$\tilde{v}^E/\tilde{v}$ × 10^2	ΔH_M × 10^2, cal g^{-1}	$T\Delta S_M$ × 10^2, cal g^{-1}	ΔG_M × 10^2, cal g^{-1}
25	1.165_8	0.03_1	$3._0$	$-5._6$	$8._5$
100	1.205_1	0.03_2	$2._0$	$-6._3$	$8._2$
150	1.230_6	0.03_7	$2._5$	$-5._4$	$7._9$

lated from its reduced temperature $\tilde{T}$ according to the methods employed in the first of the present series of papers,[1] and θ_2 is the site fraction of component 2 (see eq 9 of ref 1). The chemical potential, expressed in energy (*e.g.*, calories) per gram of component, is[2]

$$\begin{aligned}\mu_1 - \mu_1{}^0 &= (\mu_1 - \mu_1{}^0)^{\mathrm{R}} \\ &= p_1{}^* v_{sp;1}{}^* \{3\tilde{T}_1 \ln[(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + \\ &\qquad (\tilde{v}_1{}^{-1} - \tilde{v}^{-1})\} + (v_{sp;1}{}^* X_{12}/\tilde{v})\theta_2{}^2 \quad (4)\end{aligned}$$

The corresponding expression with indexes 1 and 2 interchanged holds for the chemical potential of component 2.

Numerical Calculations

Characteristic parameters for PM (component 1) and related quantities are given in Table I for three temperatures. Also included are reduced temperatures $\tilde{T} = T/T^*$ and reduced volumes $\tilde{v} = v/v^*$. These data are taken from the work of Orwoll.[4] Those at 150° are based on measurements of the density, thermal expansion coefficient, and thermal pressure coefficient of polymethylene, those at 25 and at 100° by extrapolation of results for *n*-alkanes. Owing to the limitation of experimental measurements at 25° to the homologs which are liquid at this temperature, the extrapolation is long and data for 25° are subject accordingly to greater error. Corresponding data for PIB are reported in the preceding paper.[5]

The segment site ratio s_2/s_1, required for calculation of the site fraction θ_2 from φ_2 (see eq 9 of ref 1), is estimated to be 0.72 according to the procedures employed in the preceding papers.[1,5] Inasmuch as θ_2 enters only in the term in X_{12}, which is very small, a precise value for s_2/s_1 is not required.

Calculated values of the thermodynamic mixing functions for the mixture comprising equal segment fractions of the two components are given in Table II. Also included are excess volumes calculated according to the procedures described in ref 1. The excess volumes are positive but very small. The trend with temperature is probably significant, although scarcely outside the limits set by uncertainties in the parameters at the lower temperatures. The enthalpy of mixing is positive and small; the entropy is negative and, expressed as $-T\Delta S_M$, it amounts to about twice the enthalpy. These functions combine to yield a positive free energy of mixing, which, if not large, is at least appreciable. Chemical potentials $\mu_1 - \mu_1{}^0$ and $\mu_2 - \mu_2{}^0$ relative to the pure components have also been calculated. They are positive throughout the composition range $0 < \varphi_2 < 1$.

Neighbor interactions, represented by the term in X_{12}, have little effect on the excess volume and on ΔS_M; calculations carried out with $X_{12} = 0$ yield results which depart insignificantly from those given for these quantities in Table II. Thus, $\tilde{v}^E/\tilde{v}^0$ and ΔS_M are determined almost entirely by equation-of-state contributions. The corresponding contribution to the enthalpy, on the other hand, is negative and very small. It is dominated by the positive neighbor interaction term $(v_{sp}{}^* \varphi_1\theta_2/\tilde{v})X_{12} \cong 3.5 \times 10^{-2}$ cal cc^{-1}.

The positive excess volumes and positive enthalpies of mixing are in contrast to the corresponding quantities for *n*-alkane–PIB mixtures.[1] Parameters X_{12} are positive for those systems, and substantially larger than the value for PM–PIB. Nevertheless, the contributions from X_{12} are surpassed by large negative equation-of-state terms. It is apparent that the sign of the equation-of-state contribution to the excess volume changes from negative to positive as the length of the *n*-alkane becomes very large. The sign of the equation-of-state contributions to the enthalpy and entropy remain negative, although they diminish in magnitude as the chain length increases.

The most important result is to be found in the free energy of mixing, which is unequivocally positive and approximately independent of temperature. Its magnitude is beyond the uncertainties of theory and of errors in the estimated parameters entering into the calculations. The fact that the calculated chemical potentials are positive with respect to the pure liquid components throughout the composition range denotes mutual incompatibility of these polymers *at equilibrium*. The solubility of either polymer in the other is predicted to be immeasurably low, if the molecular weights are high.

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