Thermodynamic Interactions in Isotope Blends: Experiment and Theory

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ABSTRACT: Small-angle neutron scattering (SANS) studies of binary mixtures provide χ_{NS}, a measure of thermodynamic interactions between dissimilar polymer chains, one of which is usually labeled with deuterium. For polymers differing only in isotopic substitution (isotope blends), χ_{NS} is seen to diverge strongly upward (or sometimes downward) at low concentrations of either blend component. This concentration dependence seems to vanish in the limit of large degree of polymerization N. Experimental results can be described by $\chi_{NS}(\varphi,N) = \beta + \gamma/N\varphi(1-\varphi)$, where φ is the volume fraction of deuterated polymer. For SANS from a series of blends with different φ it is shown that systematic errors in N and/or the static structure factor $S(0)$ lead to precisely the same $\chi_{NS}(\varphi,N)$ when the Flory−Huggins interaction parameter χ is constant. While results for some isotope blend systems can be accounted for with reasonable error estimates, others appear to have a real dependence of χ_{NS} on φ and N. It is suggested that these "non-Flory−Huggins" effects stem from a modified entropy of mixing that is most evident in dilute blends. The concentration dependence of $\chi_{NS}(\varphi)$ has no practical effect on macroscopic phase behavior.

Introduction

Thermodynamic interactions between polymer chains are often studied by small-angle neutron scattering (SANS), with one component of a binary blend labeled with deuterium. After the suggestion by Buckingham and Hentschel[1] that isotopic substitution would lead to small but observable repulsive interactions in polymer blends, this effect was seen in SANS experiments by Bates et al.,[2] in interdiffusion studies by Green and Doyle,[3] and in phase separation observed by Bates and Wiltzius.[4]

While the "isotope effect" is known to modify interactions between chemically dissimilar polymers, that aspect of the problem is reasonably well understood.[5,6] More perplexing are SANS results for blends of polymers differing only in isotopic substitution. These appear, at the present, to challenge our understanding of the thermodynamics of polymer−polymer blends. Consider the SANS results from Londono et al.[7] from narrow molecular weight fractions of conventional and deuterated polyethylene (PE/d-PE) shown in Figure 1. Most striking is that the apparent interaction parameter χ_{NS} has a strong dependence on blend composition, expressed as volume fraction of d-PE. The interaction parameter is obtained in the usual way, starting with the general expression for coherent cross-section per unit volume $I(q)$:

$$I(q) = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 S(q) \tag{1}$$

Here b_i/v_i is the scattering length density of the monomer in polymer i (=1, 2), and the static structure factor $S(q)$ is the absolute intensity normalized by the contrast factor in parentheses. Intensity is extrapolated to zero scattering angle ($q = 0$) to obtain $S(0)$, which is written as

$$\frac{1}{S(0)} = \frac{1}{N_1\varphi_1 v_1} + \frac{1}{N_2\varphi_2 v_2} - \frac{2\chi_{NS}}{v_0} \tag{2}$$

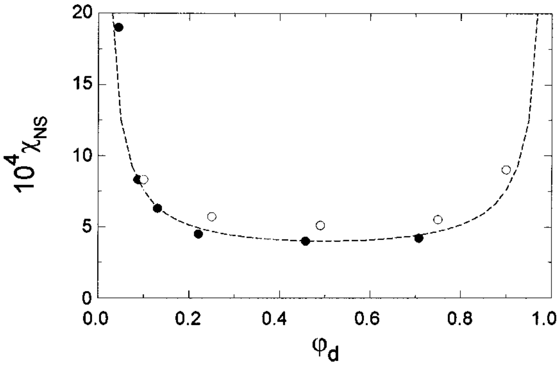

Figure 1. Dependence of χ_{NS} on blend concentration φ_d for (●) isotope blends PE/d-PE, $N \approx 4400$ (C_2H_4 monomers), $T = 155$ °C, from Londono et al.[7] and (○) model copolymer blends HPB(97)/DPB(88), $N \approx 3200$ (C_2H_4 monomers), $T = 83$ °C, from Krishnamoorti et al.[10] The dashed line is a fit of PE/d-PE data to eq 5.

N_i are (weight average) degrees of polymerization, v_i are monomer volumes, φ_i are volume fractions, and $v_0 = (v_1v_2)^{1/2}$ is the reference volume. Equation 2 is rearranged to give the apparent interaction parameter from SANS:

$$\chi_{NS} \equiv \frac{v_0}{2}\left(\frac{1}{N_1\varphi_1 v_1} + \frac{1}{N_2\varphi_2 v_2}\right) - \frac{v_0}{2S(0)} \tag{3}$$

There is no formal restriction on the method used to extrapolate intensity or $S(q)$ to $q = 0$. This step is most often done with the $q > 0$ variant of eq 2 obtained with the random phase approximation.[8] It should be emphasized that incompressible RPA theory, or, equivalently, Flory−Huggins lattice theory for a polymer−polymer blend, is invoked in the evaluation of χ_{NS} by eqs 2 and 3.

While the simplest Flory−Huggins thermodynamic model has the interaction parameter χ being independent of blend concentration φ_i and component degree of polymerization N_i, this is not required. The relation

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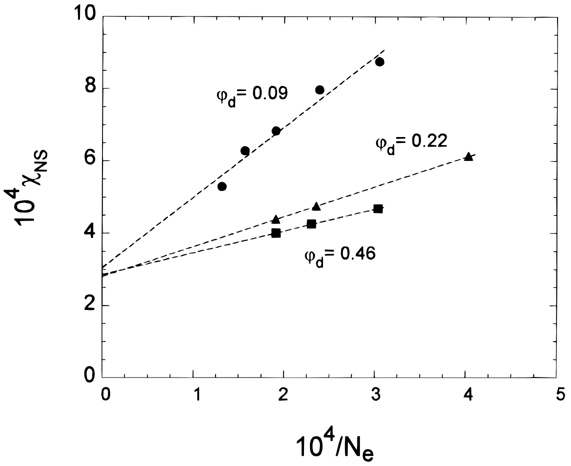

Figure 2. χ_{NS} at $T = 155$ °C versus $1/N_e$ for PE/d-PE blends having different φ_d; data from Londono et al.[7] The concentration dependence of χ_{NS} is proportional to N^{-1}.

between the thermodynamic interaction parameter χ and the SANS result is given by

$$\chi_{NS} \equiv \frac{1}{2}\frac{\partial^2(\varphi_1\varphi_2\chi)}{\partial\varphi_1\partial\varphi_2} \tag{4}$$

If and only if χ is independent of concentration, then $\chi_{NS} = \chi$. Any concentration dependence of the thermodynamic χ will lead to a larger change in the SANS quantity χ_{NS}. It was shown[9] that the ca. 4-fold increase in χ_{NS} seen in Figure 1 corresponds to a much smaller, ca. 30%, increase in χ. Another observation is that the concentration dependence of χ_{NS} is a function of N (or molecular weight) and appears to vanish in the limit of infinite N (Figure 2). Following Krishnamoorti et al.,[10] these effects can be summarized by the following empirical expression:[9]

$$\chi_{NS} = \beta + \frac{\gamma}{N_e\varphi_1\varphi_2} \tag{5}$$

Here $N_e = N_1N_2/(\varphi_1N_1 + \varphi_2N_2)$ is the appropriate average degree of polymerization for blends in which $N_1 \neq N_2$. The dashed line in Figure 1 is a fit of the PE/d-PE data to eq 5. It is emphasized that there is no theoretical foundation for eq 5, but the second "nonideal" term has a structure reminiscent of that deriving from the usual combinatorial entropy of mixing.

Also instructive is the temperature dependence of χ_{NS}. First, note that the upward curvature of $\chi_{NS}(\varphi)$ is virtually unaltered by proximity to the critical temperature (Figure 3). Blends of different φ_d each display the conventional temperature dependence $\chi_{NS}(T) = A + B/T$, but the coefficient A (implying an entropic contribution to the interaction) has by far the greatest sensitivity to concentration (Figure 4).

Although the data of Londono et al.[7] on PE/d-PE are the most comprehensive in terms of φ_d, N, and T dependence, similar results are seen with most isotope blends. The first report of upward curvature of $\chi_{NS}(\varphi)$ was by Bates et al.[11] for PEE/d-PEE and PVE/d-PVE; those data closely resemble the effect shown in Figure 1. (PEE is equivalent to atactic poly(butene-1), having an ethyl branch on every second backbone carbon; PVE has unsaturated vinyl branches.) Krishnamoorti[12] has recently studied isotope blends of 1,4-polyisoprene, poly(ethylene oxide), and poly(methyl methacrylate); in each case the interaction parameter from neutron scattering increases noticeably when $\varphi_d \leq 0.2$. For polystyrene isotope blends the "parabolic" curvature of χ_{NS} is downward, an effect confirmed by two groups.[7,13] Noteworthy is the finding by Schwahn et al.[13] that χ_{NS} is negative for $\varphi_d < 0.2$, a point to be considered later. A summary of these observations is presented in Table 1. Proximity to the critical point is indicated by $N_e\chi_{NS}(0.5) < 2$, and the magnitude and sense of curvature is indicated by the ratio $\chi_{NS}(0.1)/\chi_{NS}(0.5)$. The combined error factor "c" is defined below.

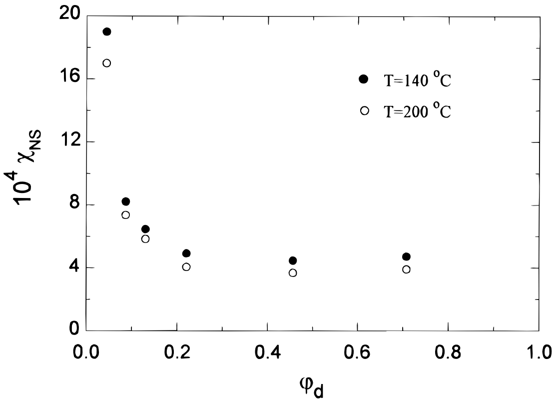

Figure 3. $\chi_{NS}(\varphi)$ for PE/d-PE, $N \approx 4400$, at two temperatures above the critical temperature $T_c = 132$ °C (405 K); data from Londono et al.[7] Concentration dependencies of χ_{NS} are indistinguishable at $T/T_c = 1.02$ (●) and at $T/T_c = 1.17$ (○).

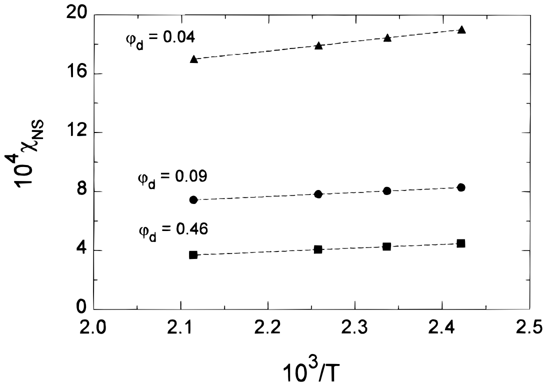

Figure 4. Temperature dependence of $\chi_{NS}(T) = A + B/T$ for PE/d-PE of different φ_d, $N \approx 4400$; data from Londono et al.[7] The increase in χ_{NS} at low φ_d seen in Figures 1 and 3 are associated with larger "A".

Table 1. Concentration Dependence of χ_{NS} in Polymer Isotope Blends

blend	T (K)	$10^{-3}N_e$	$N_e\chi_{NS}(0.5)$	$\frac{\chi_{NS}(0.1)}{\chi_{NS}(0.5)}$	c	ref
PEE/d-PEE	299	1.50	1.3	1.78	1.4	11
PVE/d-PVE	310	1.50	1	1.67	1.3	11
PE/d-PE	428	4.36	1.9	1.88[a]	1.5	7
PI/d-PI	300	1.18	0.9	1.31	1.1	12
PEO/d-PEO	347	2.39	1.1	1.24[a]	<1.1	12
PMMA/d-PMMA	381	1.58	0.5	1.32	<1.1	12
PS/d-PS	433	9.91	1.8	0.80[b]	0.9	7
PS/d-PS	439	9.47	1.6	−0.65[a]	0.6	13

[a] For $\varphi_d = 0.09$. [b] For $\varphi_d = 0.125$.

Excepting PS/d-PS, the behavior in Figure 1 can be considered typical for weakly interacting blends, i.e., those lacking specific interactions between component polymers. Expanding our scope to include model polyolefins, where h-polymers and d-polymers differ in chemical microstructure as well as isotopic substitution, SANS behavior is generally similar. In the majority of cases one again sees symmetric upward curvature of χ_{NS}, as illustrated in Figure 1 for the pair of saturated polybutadienes HPB(97)/DPB(88) from work by Krishnamoorti et al.;[10] numbers in parentheses are percent 1−2 additions of butadiene that lead to ethyl branches along the chain. In some cases this behavior is skewed by a monotonic increase of χ_{NS} with larger concentration of the more branched component. Blends of model alternating copolymers with the same amount of branching, one methyl branched and the other ethyl branched, have χ_{NS} independent of concentration over the range $\varphi_d = 0.25-0.90$.[14] A constant $\chi(\varphi)$ has recently been reported for lightly branched d-PE blended with an alternating copolymer of ethylene and propylene for $\varphi_d = 0.1-0.9$.[15]

Hence SANS experiments show that the apparent interaction parameter χ_{NS} and, by inference, the thermodynamic χ depend on blend concentration in a manner that is not understood. In this paper we consider certain experimental and theoretical aspects that appear to have been overlooked.

Experimental Issues

The SANS result χ_{NS} is established by the difference between a calculated quantity (the first term on the right-hand side of eq 3, sometimes designated χ_s, the spinodal value of χ) and an experimental quantity (the reciprocal structure factor modified by $v_0/2$). However, be reminded that χ_s depends on independently measured values of N_i. Both terms increase as the blend concentration is changed from $\varphi_i \approx 0.5$, diverging as φ_i approaches zero. Thus χ_{NS} for dilute blends is established by the difference between two large numbers, leading to less precision in χ_{NS} when the usual random errors associated with N_i and $S(0)$ are considered.[7,10]

Experimental uncertainties are manifested differently when a single pair of polymers are blended to obtain different φ_d and studied at one temperature, the condition for establishing $\chi_{NS}(\varphi)$. Here one is concerned with *systematic* errors, most likely incorrect N_i (molecular weight error) and $S(0)$ (mass density, deuterium fraction and/or absolute intensity calibration errors). Taylor-Maranas et al.[16] mentioned that these can cause a "parabolic" dependence of χ_{NS} on φ, an idea pursued here in more detail. The analysis can be made most simply for symmetric blends ($N_1 = N_2 = N$) in which the <1% change in molar volumes caused by deuterium labeling is ignored ($v_1 = v_2 = v_0 = v$). We proceed by assuming that the Flory−Huggins approach to polymer blends is obeyed, i.e., for error-free experiments one obtains

$$\frac{v}{2S(0)} = \frac{1}{2N\varphi_1\varphi_2} - \chi \tag{6}$$

Here the Flory−Huggins interaction parameter χ is independent of φ and N; under these conditions eq 3 clearly returns $\chi_{NS} = \chi$. But now we allow for systematic errors so that the experimental $N' = N/a$ and $S'(0) = bS(0)$. Evaluation of χ_{NS} is done in terms of potentially incorrect quantities N' and $S'(0)$:

$$\chi_{NS} \equiv \frac{1}{2N'\phi_1\phi_2} - \frac{v}{2S'(0)} \tag{7}$$

Substituting for N' and S' with eq 6 we obtain

$$\chi_{NS} = \frac{\chi}{b} + \frac{a - 1/b}{2N\varphi_1\varphi_2} \tag{8}$$

The parallel to eq 5 is obvious, where $\beta = \chi/b$ and $\gamma = (a - 1/b)/2$. Hence we have shown that systematic errors, which must exist for both degree of polymerization N and normalized intensity $S(0)$, *may* cause the type of concentration dependence of χ_{NS} that is seen so often. This realistic assessment of the SANS experiment will lead to a perfectly smooth variation of χ_{NS} with φ. Random errors, e.g., those resulting from background subtraction, sample thickness, etc. for blends of each φ_d, will cause erratic departures from eq 8, but these appear to be small.

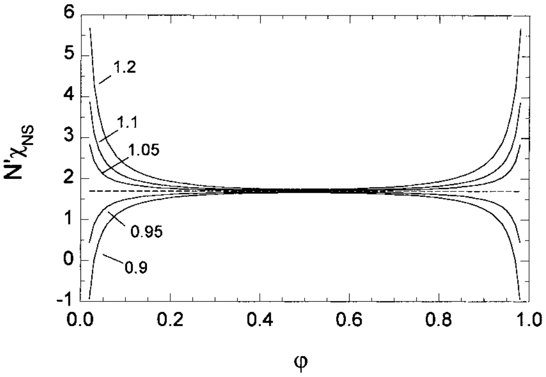

Figure 5. Error model results $N'\chi_{NS}$ versus φ for $N\chi = 1.7$, with indicated values of c.

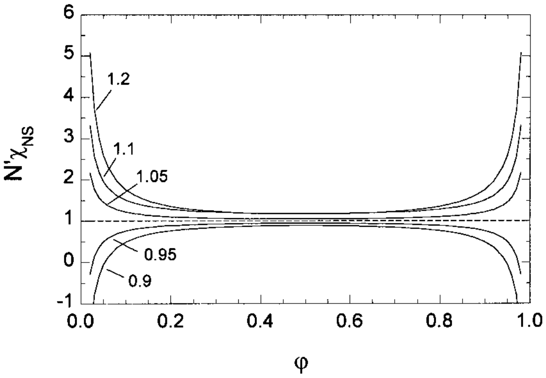

Figure 6. Error model results $N'\chi_{NS}$ versus φ for $N\chi = 1.0$, with indicated values of c.

Equation 8 can be rewritten in terms of a combined error factor $c = ab$ as

$$N'\chi_{NS} = \frac{N\chi}{c} + \frac{c - 1}{c}\,\frac{1}{2\varphi_1\varphi_2} \tag{9}$$

The left-hand side of eq 9 is expressed in terms of N' used to determine χ_{NS}, thus corresponding to experiment. Some examples of systematic error effects are shown in Figure 5 and Figure 6 for representative values of $N\chi = 1.7$ and 1.0. These serve to emphasize that positive or negative curvature will result when $c > 1$ or $c < 1$, respectively. Note that negative values of χ_{NS} follow when $c < 1$ and that all curvature effects are more pronounced for smaller $N\chi$ (lower molecular weight or substantially higher temperature).

Experiments on PE/d-PE indicate that $\chi_{NS} \sim 1/N$ for constant φ_d (Figure 2). The structure of eq 8 indicates the same response, as illustrated in Figure 7. Not so obvious is the effect of systematic errors on the temperature dependence of χ_{NS}. Here we assume the thermodynamic $N\chi = B/T$, which is varied (at constant N) over an appropriate range. The result in Figure 8, again for $c = 1.2$, recovers the experimental trends shown in Figure 4. Upward shifts of parallel lines for lower φ_d enhance the apparent entropic component "A" of $\chi_{NS}(T) = A + B/T$. Notice that $N'\chi_{NS}(0.5) = 2$ at exactly the true critical temperature when $N\chi = 2$; this point is considered below. For the case $c < 1$ the parallel lines are shifted downward, just as seen by Schwahn et al.[13] with polystyrene isotope blends.

Hence it is demonstrated that the "anomalous" SANS results from isotope blends, vis. upward or downward curvature of χ_{NS} that scales with $1/N$ and "entropic" coefficients A that depend on φ, can be generated by systematic errors in

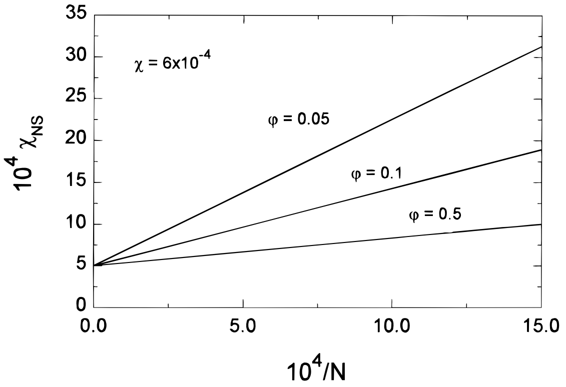

Figure 7. Error model results χ_{NS} versus $1/N$ for different values of φ. Here $c = 1.2$ and the constant $\chi = 6 \times 10^{-4}$. Compare to Figure 3.

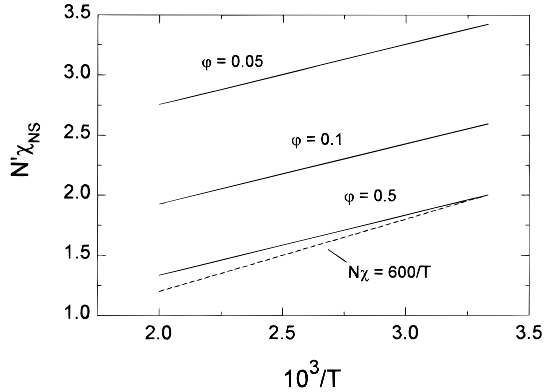

Figure 8. Error model results $N'\chi_{NS}$ versus $1/T$ for different values of φ. Here $c = 1.2$ and $N\chi = 600/T$. Compare to Figure 4.

either degree of polymerization ($N' \neq N$) or structure factor ($S'(0) \neq S(0)$).

Discussion

The concentration dependence of χ_{NS} has been most often attributed to oversimplifications in the Flory–Huggins treatment of binary solutions. One can envision two classes of refinements: (1) those involving general effects, e.g., nonrandom mixing or nonideal entropy of mixing, which may yield universal corrections manifested in a common $\chi_{NS}(\varphi,N)$, or (2) those involving system specific corrections (e.g., enthalpic interactions or volume changes varying with φ) that would allow $\chi_{NS}(\varphi,N)$ to have any sort of behavior, including upward or downward curvature. A third possibility is (3) the simplest Flory–Huggins thermodynamic model is correct, and the observed $\chi_{NS}(\varphi,N)$ results from imprecise measurements, as described in the preceding section. The experimental record summarized in Table 1 precludes (1), a general modification of solution thermodynamics. This conclusion is based not only on the qualitative distinction between PS/d-PS and the other isotope blends but also on the various magnitudes of upward curvature summarized in Table 1. Any general approach must involve a combination of (1) and (3) to account for varied results. While a system-specific modification of blend thermodynamics (2) is always possible, it is difficult to imagine what differentiates PS so strongly from the other polymers. We first consider the plausibility of the systematic error model and then return to theoretical implications.

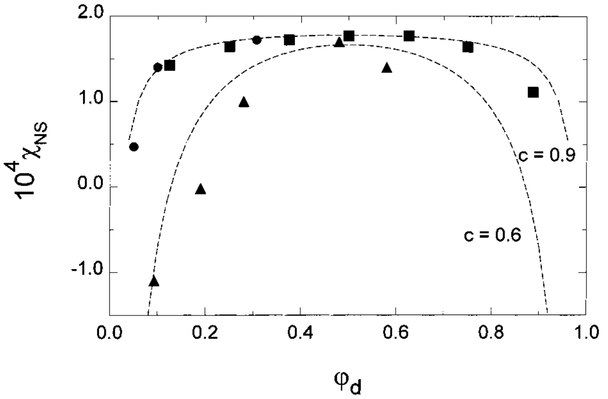

Figure 9. Concentration dependence of χ_{NS} in PS/d-PS glasses annealed at $T \approx 160$ °C. $N_e\chi_{NS} = 1.75$ system as analyzed by Londono et al.[7] (■). Higher molecular weight $N_e\chi_{NS} = 2.5$ system as analyzed by Londono et al.[7] (●). Results from Schwahn et al.[13] (▲) with original (incorrect) molecular weights. Dashed lines are approximate fits to the error model with $c = 0.9$ and $c = 0.6$.

A. Error Estimates. Note that the concentration dependence of χ_{NS} in eq 9 is a function of both the error factor c and the size of $N\chi$. The apparent combined error factor c associated with a particular experimental system can be estimated from the observed ratio of χ_{NS} at two values of φ_d together with $N_e\chi_{NS}$ at $\varphi_d \approx 0.5$. Table 1 includes these estimates for the eight sets of results on seven different isotope blend systems. We focus for the moment on those displaying upward curvature of $\chi_{NS}(\varphi)$, here interpreted as resulting from $c > 1$. The data for PI, PEO, and PMMA are all accounted for by error factor $c \leq 1.1$, which is a reasonable value. For instance, the intensity calibration could be high by 5% ($b = 1.05$) and molecular weights low by about the same factor ($a = 1.05$). The concentration dependence reported for PEE, PVE, and PE requires $c \approx 1.3$–1.5, which is admittedly beyond the range $c = 0.9$–1.1 corresponding to ca. ±5% errors usually associated with measurements of molecular weight and absolute intensities.[7,10]

Data for PS/d-PS are revealing in this regard. This system is unique in many ways; it was studied by different groups, shows downward curvature of χ_{NS}, and was investigated in the glassy state. Results from Schwahn et al.[13] and Londono et al.[7] are plotted in Figure 9, along with data for a second, higher N_e PS/d-PS system.[7] Data from Londono et al. are described nicely by $c = 0.9$, while those from Schwahn are quite different and require $c \approx 0.6$ as a rough assessment of the combined errors if it is assumed that χ is constant. Note that this latter factor implies systematic errors of the same absolute size as those for PEE, PVE, and PE ($c \approx 1.4$), considerably beyond the conventionally accepted range of $0.9 \leq c \leq 1.1$. In this instance, however, later studies showed that the apparent molecular weights of both conventional and perdeuterated polystyrene were nearly 30% too large.[17] With revised N' the first term on the right side of eq 7 is larger and $\chi_{NS}(\varphi)$ closely resembles the Londono results ($c \approx 0.9$); χ_{NS} is no longer negative for low φ_d. It is not known if the downward curvature of $\chi_{NS}(\varphi)$ in PS/d-PS glasses is real or derives from some residual errors. The point to be made is that, in at least one case, large systematic errors do occur.

Systematic errors are by nature more difficult to detect and assess than random errors. It is fair to ask if another experimental result can be brought to bear on the problem. One immediately thinks of macroscopic phase separation or "cloud point" measurements, most unambiguously done with blends having the critical concentration $\varphi_c \approx 0.5$. Unfortunately, this test will return a result completely consistent with "erroneous" SANS measurements of χ_{NS} in the one-phase state. Consider the extreme example $c = 1.5$ when the apparent molecular weight is 33% too low ($a = 1.5$) or the less likely condition when intensities are 50% too large ($b = 1.5$). Equation 9 becomes $N'\chi_{NS} = (N\chi + 0.25/\varphi_1\varphi_2)/1.5$, which equals 2.0 at precisely the true critical point ($N\chi = 2$ and $\varphi_1 = \varphi_c = 0.5$). Figure 8 presents another example for $c = 1.2$. Hence phase separation of critical blends will occur at exactly the temperature predicted from measurements of $\chi_{NS}(T)$. Experiments with off-critical blends can yield volume fractions and/or phase concentrations[18,19] that can in principle test the concentration dependence of the thermodynamic χ and hence the significance of $\chi_{NS}(\varphi)$. However, the shape of the binodal is scarcely altered, even when χ has a (small) φ dependence consistent with the (large) concentration dependence of χ_{NS} in Figure 1,[9,10] meaning that phase-separated structures cannot practically distinguish between real and error-generated concentration dependence of χ_{NS}. While this situation is frustrating from the perspective of assessing the reality of $\chi_{NS}(\varphi)$, it also means that phase behavior can be interpreted confidently by the Flory–Huggins model with interaction parameters (constant $\chi = \chi_{NS}(0.5)$) measured for symmetric blends.

We believe that it is more than coincidental that the empirical form of $\chi_{NS}(\varphi,N)$ summarized in eq 5 is exactly the same as eq 8 expected for systematic errors. At issue are two questions: Why are all curvatures upward, except for PS/d-PS? Can the factor c be as large as 1.5? Possible answers involve details of molecular weight measurement and intensity calibration that are beyond the scope of this work. It is suspected that molecular weight measurements may vary by more than usually quoted. We refer to the 26% change in N_e for PS/d-PS mentioned previously.[17] PE/d-PE, for which χ_{NS} has the largest upward curvature, has molecular weights determined by gel permeation chromatography (GPC). The author is aware of very careful measurements on a standard reference material PE for which M_w from GPC was variously reported as 170k[20] and 140k,[21] a 20% difference that is two-thirds that needed to account for $c = 1.5$ for that system (Table 1).

The exact role of experimental errors in evaluation of χ_{NS} cannot be established at present. Reasonable values of $c = 0.9–1.1$ account for the downward curvature in PS and upward curvature in PI, PEO, and PMMA; such "moderate" changes of χ_{NS} with φ_d are not reliable evidence for deviations from the Flory–Huggins model. Systems with stronger upward curvature (PE, PVE, PEE, and model polyolefins) can also be accommodated by systematic errors, but only if $c \geq 1.3$, which is beyond the normally accepted range. It is likely (but not certain) that the SANS result $\chi_{NS}(\varphi,N)$ is real in these cases. However, the size of changes of χ_{NS} with φ_d and N are subject to expected effects from conventional $c = 0.9–1.1$. Even for these systems it is disquieting that *all* features of "non-Flory–Huggins" behavior are self-consistently reproduced by the error model.

B. Theoretical Approaches. Accepting that the observed $\chi_{NS}(\varphi,N)$ are correct (not the result of systematic errors) in at least some systems, behavior appears dominated by entropic effects in the free energy of mixing. Symmetric changes around $\varphi_d = 0.5$ and vertical shifts of $\chi_{NS}(1/T)$ both testify to this, as does the fact that "anomalous" effects vanish as $1/N$ (eq 5). This entropic nature of "non-Flory–Huggins" results was noted by Londono et al.[7] but has not been emphasized in the many theoretical studies that address the concentration dependence of χ_{NS}. Those have focused on nonrandom mixing associated with concentration fluctuations near the critical point and on density fluctuations (compressibility), both of which are ignored in the Flory–Huggins approach used to define χ_{NS} (eq 3). We make no attempt to review comprehensively the large volume of literature that has addressed these issues for polymer blends but consider those treatments most applicable to isotope blends (structurally identical chains), with emphasis on the divergence of χ_{NS} at low concentrations.

With the classical model, concentration fluctuations in the one-phase liquid are predicted to diverge in both amplitude and length scale as the critical point (or any point on the spinodal) is approached, typically by decreasing temperature. These are characterized by deviations from random mixing and the formation of large concentration gradients. The former modify both enthalpy and entropy of the mixed state, and the latter leads to an additional enthalpic gradient energy penalty. The consequence is to damp the magnitude of concentration fluctuations, meaning that $S(0)$ is reduced from its classical value, hence $\chi_{NS}(0.5)$ is less than the Flory–Huggins χ, which represents the enthalpy of binary interactions. At a fixed temperature these fluctuations diminish as global concentration is changed from $\varphi_c \approx 0.5$, and one expects χ_{NS} to rise toward χ as φ is reduced. Related expectations are that the φ dependence of χ_{NS} becomes smaller as the temperature is increased from T_c and that the importance of excess energy associated with fluctuations becomes smaller for larger chains. The role of fluctuations in incompressible polymer blends has been addressed by two groups. In one case χ_{NS} is predicted to have a very small *downward* curvature,[22] while the other analysis has χ_{NS} diverging *upward*,[11] similar to experiments in Figure 1. The fact that two treatments of the same problem lead to qualitatively different results, neither of which is expected from a general consideration of fluctuations, is disturbing.[23] We note also that experiments on PE/d-PE show that $\chi_{NS}(\varphi)$ is unchanged by proximity to the critical temperature (Figure 3), indicating that the observed effect does not derive from fluctuations of this sort.

The role of compressibility in blend thermodynamics has led to some confusion. At issue is the effect of voids or free volume, a third component with volume fraction $\phi_v \approx 0.1$, on the blend free energy and χ_{NS}. For isotope blends one expects ϕ_v to be effectively independent of φ_d because compressibilities of the pure polymers and the blend are very similar. A number of treatments of compressible isotope blends have indicated that χ_{NS}, defined by the "incompressible" approach embodied in eq 3, diverges either upward[24–26] or downward[27–29] at low concentrations of either component. It is likely that these calculated results, which indeed mimic experimental $\chi_{NS}(\varphi,N)$ effects, result from subtle problems encountered when describing compressible and incompressible blends with lattice models. In Appendix 1 it is shown that a constant volume fraction of voids does not lead to divergent behavior of χ_{NS} when $S(0)$ and χ_s

are defined consistently, as is done with analysis of experimental data. This finding is in accord with recent analyses of systems in which compressibility is allowed to vary a small amount, as in isotope blends. Taylor-Maranas et al.[16] show with a lattice-fluid model that compressibility does not modify the SANS intensity at small φ; the only way to account for observed $I(0)$ or $S(0)$ is to increase the thermodynamic χ for dilute blends. Kumar et al.[30] use general thermodynamic arguments to show that χ_{NS} is similarly unaffected by free volume of the magnitude seen in "weakly interacting" polymer blends. Hence compressibility itself (components and blend of same or similar compressibility or void content) cannot account for the observed concentration dependence of χ_{NS} in isotope blends.

Fluctuations and compressibility are both included in thermodynamic approaches more sophisticated than the Flory–Huggins model. Singh et al.[31] have employed the polymer reference interaction site model (PRISM) to address the concentration dependence of χ_{NS} in structurally symmetric (isotope) blends. Density or void fraction is independent of blend concentration, as expected for weakly interacting systems, in this off-lattice calculation. They find that χ_{NS} invariably increases as the blend concentration is changed from $\varphi_c = 0.5$. The magnitude of the change depends on model details but is smaller for larger N and less compressible (more dense) systems. For $N \geq 1000$ and the highest liquid density, the calculated ratio $\chi_{NS}(0.1)/\chi_{NS}(0.5) \approx 1.1$, which is much smaller than the reliable experimental effects in Table 1. More importantly, there is no indication that $\chi_{NS}(\varphi)$ diverges at low φ, contrary to observed behavior. Quite interesting in this regard is the recent work of Melenkevitz[32,33] using off-lattice optimized cluster theory (OCT) to model isotope blends, specifically the PE/d-PE system of Londono et al.[7] Here again fluctuations and constant compressibility are included. The model mimics experiment in many ways, with $\chi_{NS}(\varphi,N)$ described by the empirical eq 5; both the divergence of $\chi_{NS}(\varphi)$ and the $1/N$ dependence of $\chi_{NS}(N)$ are captured. Calculations were done at two temperatures, permitting one to determine that the apparent increase in χ_{NS} has entropic character (A increases when φ is altered from 0.5). Changes of χ_{NS} in the model are, however, about 10% of the observed ones, i.e., $\chi_{NS}(0.1)/\chi_{NS}(0.5) \approx 1.1$ rather than the ratio of 1.8 in Figure 1. Such calculated effects would be virtually impossible to measure with confidence, as they are of the same size as those generated by a combined error factor $c < 1.03$.

It appears unlikely that the large concentration dependence of $\chi_{NS}(\varphi)$ seen for example in Figures 1 and 3 results from either fluctuations or compressibility. Stipulating that such experiments are not strongly compromised by systematic errors, one is led to examine χ_s or the term in parentheses in eq 3. Experimental results suggest that this term, which derives from the ideal entropy of mixing, is inadequate, with discrepancies being larger at low concentrations. Flory[34] clearly identified limitations of the lattice model for calculating ΔS_m in dilute solutions, where local concentrations are quite different from the global volume fraction φ. In blends one expects a similar situation at concentrations below $\varphi^* = 3v/(4\pi N^{1/2} l^3)$, where one (labeled) chain with radius of gyration $R_g = N^{1/2} l$ is completely solvated by chains of the other type (unlabeled), but effects may be seen at higher φ. The point is that in dilute blends there are additional concentration fluctuations, not accounted for in Flory–Huggins or related theories, that arise purely from chain connectivity.

The SANS result from eq 3 is based on the ideal entropy of mixing calculated per lattice site or liquid volume element v_0:

$$\frac{-\Delta S_m^{id}}{k} = \frac{\varphi_1}{N_1} \ln \varphi_1 + \frac{\varphi_2}{N_2} \ln \varphi_2 \qquad (10)$$

This expression equals zero for either pure component ($\varphi_i = 0$) and furthermore is the *maximum* entropy for a randomly mixed blend with concentrations φ_1 and $\varphi_2 = 1 - \varphi_1$. Any modification for dilute blend effects will reduce the magnitude of ΔS_m below that for ΔS_m^{id} when $\varphi_i \sim \varphi^*$, and ΔS_m must approach 0 when $\varphi_i = 0$. Given these constraints, the concentration derivative of entropy should be less than that for the ideal case: $\partial \Delta S_m/\partial \varphi_i < \partial \Delta S_m^{id}/\partial \varphi_i$. The second derivative is needed for calculating $S(0)$. We assert without proof that the second concentration derivative of ΔS_m in dilute blends is smaller than the classical χ_s; an example based on the empirical form of $\chi_{NS}(\varphi,N)$ is given in Appendix 2. There it is also shown that downward curvature of $\chi_{NS}(\varphi)$ is inconsistent with this thermodynamic argument.

Systems in Table 1 have φ^* in the range 0.015 (PE/d-PE) to 0.085 (PEE/d-PEE). Since effects are seen at concentrations up to $10\varphi^*$ in some cases (e.g., Figure 1), a gradual crossover is implied. There is no apparent relation between φ^* and the magnitude of $\chi_{NS}(\varphi)$ changes. It is possible that the strength of the "isotope effect" is operative here. Flory[34] demonstrated years ago that repulsive interactions in a polymer/solvent system can lead to an apparently ideal entropy of mixing that defines the "Θ condition". Similar arguments should apply to polymer–polymer blends, and the different upward curvatures, assuming they are real, may reflect different amounts of "compensation" toward the equivalent of ideal mixing. We are not aware that this approach to the concentration dependence of χ_{NS} has been taken, although it may be present in the OCT study mentioned above. Melenkevitz and Curro[32] find that nonrandom mixing in their model of the PE/d-PE system extends over $\sim 3R_g$ for a blend near the critical point ($\varphi = 0.5$), which is expected from fluctuations. More interesting is that nonrandom mixing has decayed by only ~50% when $\varphi = 0.1$. As this dilute blend is far from the spinodal, nonrandom mixing could be a manifestation of the postulated dilute blend effect.

Conclusions

There is no doubt that the popularity of the Flory–Huggins approach to polymer thermodynamics derives in large measure from its simplicity. While this model is not expected to apply to all systems, isotope and other weakly interacting blends would appear to conform most closely to the assumptions of equal monomer volumes and a concentration independent interaction parameter χ. On this basis it is surprising that SANS experiments on such "model systems" indicate strong departures from regular solution behavior.

Taken at face value, the concentration, chain length, and temperature dependencies of χ_{NS} in isotope blends have every characteristic of originating from the entropy of mixing. It is unfortunate that unavoidable, and in many cases reasonable, systematic errors in the SANS experiment generate exactly the same effects. The most conservative position is that the magnitude and even the sign of changes in $\chi_{\mathrm{NS}}(\varphi)$ are uncertain. Nevertheless, the dominance of experimental reports of upward curvature of $\chi_{\mathrm{NS}}(\varphi)$ implies that such responses are genuine reflections of the thermodynamics of the mixed state. This sort of “non-Flory−Huggins” behavior does not affect the relation between χ_{NS} measured for critical blends and macroscopic phase separation.[9,10]

We are aware of no thermodynamic model that accounts for the type and magnitude of $\chi_{\mathrm{NS}}(\varphi,N)$ in isotope and other weakly interacting polymer blends. A qualitative case is made for the modified entropy of mixing associated with chain connectivity, which is expected to be most important in dilute blends. Any approach must account for system specific effects, as the conspicuous curvature of $\chi_{\mathrm{NS}}(\varphi)$ appears to vary from moderate (PI, PEO, PMMA) to strong (PE, PEE, PVE). We conclude by reiterating that the symmetric concentration dependence of χ_{NS} in isotope blends, where the only “asymmetry” is the substitution of deuterium for hydrogen, presents an ongoing challenge to our understanding of the thermodynamics of polymer mixtures. There are apparent departures from the ideal entropy of mixing which, although they vanish in the limit of infinite N, are system specific. Our ability to handle more complex mixtures[10,14,15] is compromised in the absence of an explanation for this “isotope effect”.

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Appendix 1

The effect of compressibility (presence of voids) on the analysis of thermodynamics and scattering is considered for a system of unit volume composed of polymer 1 (volume fraction ϕ_1), polymer 2 (ϕ_2), and voids (ϕ_{v}) on a lattice of N_{c} cells of volume $v_{\mathrm{c}} = 1/N_{\mathrm{c}}$. Following Freed,[24] one can write the free energy of mixing per lattice cell as

$$\frac{\beta\Delta F}{N_{\mathrm{c}}} = \phi_{\mathrm{v}} \ln \phi_{\mathrm{v}} + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \phi_1\phi_2\chi_{12} + \phi_1\phi_{\mathrm{v}}\chi_{1\mathrm{v}} + \phi_2\phi_{\mathrm{v}}\chi_{2\mathrm{v}} \quad (11)$$

Here $\beta = 1/kT$, N_i is degree of polymerization of polymer i, and $\phi_1 + \phi_2 + \phi_{\mathrm{v}} = 1$. The χ_{ij} are the usual normalized exchange energies for interactions between dissimilar monomers, here including voids. Assuming for simplicity that void fraction ϕ_{v} is independent of blend concentration (expected to be approximated closely for isotope blends), the static structure factor is given by[35]

$$\frac{v_{\mathrm{c}}}{S_{\mathrm{c}}(0)} = \frac{\partial^2(\beta\Delta F/N_{\mathrm{c}})}{\partial{\phi_1}^2} = \frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} - 2\chi_{12} \quad (12)$$

The same compressible system (polymers plus voids) can be treated on an “incompressible” lattice of the same unit volume but having fewer cells $N_{\mathrm{inc}} = (1 - \phi_{\mathrm{v}})N_{\mathrm{c}}$ of larger volume $v_{\mathrm{inc}} = v_{\mathrm{c}}/(1 - \phi_{\mathrm{v}})$. The free energy of mixing ΔF is unchanged, but it is written in terms of the incompressible lattice as

$$\frac{\beta\Delta F}{N_{\mathrm{inc}}} = \frac{\varphi_1}{N_1} \ln \varphi_1 + \frac{\varphi_1}{N_1} \ln \varphi_1 + \varphi_1\varphi_1\chi_{12}^{\mathrm{inc}} \quad (13)$$

Here the blend concentration is expressed in terms of nominal volume fractions $\varphi_i = \phi_i/(1 - \phi_{\mathrm{v}})$ where $\varphi_1 + \varphi_2 = 1$ and χ_{12}^{inc} represents the free energy in excess of the combinatorial entropy of mixing. While the third term in eq 13 is associated with pairwise contacts between polymer 1 and polymer 2, χ_{12}^{inc} is not the same as χ_{12} in eq 11. The static structure factor is written as in Flory−Huggins theory, assuming χ_{12}^{inc} is independent of blend concentration, as

$$\frac{v_{\mathrm{inc}}}{S_{\mathrm{inc}}(0)} = \frac{\partial^2(\beta\Delta F/N_{\mathrm{inc}})}{\partial{\varphi_1}^2} = \frac{1}{N_1\varphi_1} + \frac{1}{N_2\varphi_2} - 2\chi_{12}^{\mathrm{inc}} \quad (14)$$

Either eq 12 or eq 14 may be used to evaluate χ_{12} or χ_{12}^{inc}, respectively. The relation between them is obtained by rewriting eq 14 as

$$\frac{\partial^2(\beta\Delta F/N_{\mathrm{inc}})}{\partial{\varphi_1}^2} = \frac{N_{\mathrm{c}}}{N_{\mathrm{inc}}} \frac{\partial^2(\beta\Delta F/N_{\mathrm{c}})}{\partial{\phi_1}^2}\left(\frac{\partial\phi_1}{\partial\varphi_1}\right)^2 \quad (15)$$

Substitution from eqs 12 and 14 leads to

$$\frac{v_{\mathrm{inc}}}{S_{\mathrm{inc}}(0)} = (1 - \phi_{\mathrm{v}})\frac{v_{\mathrm{c}}}{S_{\mathrm{c}}(0)} \quad (16)$$

or, using the right-hand sides of eqs 12 and 14:

$$\chi_{12}^{\mathrm{inc}} = (1 - \phi_{\mathrm{v}})\chi_{12} \quad (17)$$

With the identity $v_{\mathrm{c}} = (1 - \phi_{\mathrm{v}})v_{\mathrm{inc}}$, eq 16 returns unequal structure factors for the two models, i.e. $S_{\mathrm{c}}(0) = (1 - \phi_{\mathrm{v}})^2 S_{\mathrm{inc}}(0)$. This inequality of structure factors, which has not been generally appreciated, derives from the “contrast” factor in parentheses in eq 1 of the text. For a compressible model the scattering length densities are based on “hard core” volumes (v_{c}) rather than the larger nominal molar volumes (v_{inc}) of monomers. Either side of eq 16 is consistent with a sample having a coherent cross section per unit volume $I(0)$, which can be analyzed according to compressible or incompressible lattice models.

The only difference between the “incompressible” result χ_{12}^{inc} and the “compressible” χ_{12} is the factor $(1 - \phi_{\mathrm{v}})$ in eq 17. This is readily understood in terms of the heat of mixing from 1−2 contacts in the two models, $\beta\Delta H_{\mathrm{m}} = N_{\mathrm{c}}\phi_1\phi_2\chi_{12} = N_{\mathrm{inc}}\varphi_1\varphi_2\chi_{12}^{\mathrm{inc}}$, which leads directly to eq 17. Because voids are not considered explicitly, the factor $N_{\mathrm{inc}}\varphi_1\varphi_2$ in the incompressible model overestimates the number of 1−2 contacts, so the interaction parameter χ_{12}^{inc} must be reduced to correct for this overcounting.

In summary, the mere presence of a void population (constant $\phi_{\mathrm{v}} > 0$) alters neither the thermodynamics nor scattering of a binary blend in a significant manner. Any comparison of analyses by compressible and incompressible models should account properly for differences in structure factors $S(0)$ and cell or reference volumes v. When this is done, the concentration independent interaction energy embodied in χ (or χ_{NS}) is affected only by a constant factor $(1 - \phi_{\mathrm{v}})$. There is no divergence of $\chi_{\mathrm{NS}}(\varphi)$ that can be attributed to compressibility of an

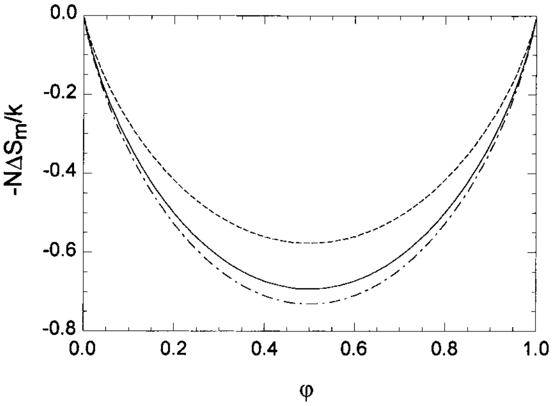

Figure 10. Entropic contribution to the free energy of mixing as a function of blend concentration for ideal mixing (—) and the empirical eq 12 for $\gamma = 0.167$ (- - -) and for $\gamma = -0.055$ (•—•).

experimental blend. It is obvious, however, that mixing elements of the two approaches, e.g., using a compressible $v_c/S_c(0)$ on the right-hand side of eq 3, when the combinatorial entropy terms are based on in incompressible model, will cause a meaningless divergence of "χ_{NS}" at low concentrations. In fact, this is just another example of a systematic error (from theory, not experiment) affecting $S(0)$ and hence $\chi_{NS}(\varphi)$. The need for consistent application of a particular model has been emphasized by Taylor et al.[26]

Appendix 2

The empirical expression for $\chi_{NS}(\varphi,N)$ in eq 5 can be integrated twice over φ_1 to obtain the following expression for the thermodynamic χ consistent with the Flory–Huggins model:[9,10]

$$\chi = \beta - \frac{2\gamma}{N_e\varphi_1\varphi_2}(\varphi_1 \ln \varphi_1 + \varphi_2 \ln \varphi_2) \qquad (18)$$

The second term can be assigned to the departure from ideal entropy of mixing, leading to a phenomenological equation for symmetric blends ($N_1 = N_2 = N$):

$$\frac{-N\Delta S_m}{k} = (1 - \gamma)(\varphi_1 \ln \varphi_1 + \varphi_2 \ln \varphi_2) \qquad (19)$$

This modified version of the entropy of mixing is plotted in Figure 10 for $\gamma = 0.17$ (equivalent to $c = 1.5$ for PE/d-PE) and $\gamma = -0.055$ (equivalent to $c = 0.9$ for PS/d-PS). Be reminded that there is no theoretical basis for the particular form of eq 19, which derives from experimental measurements of $\chi_{NS}(\varphi,N)$. For $\gamma > 0$ (upward curvature) this model reflects the reduced entropy of mixing expected from general consideration of chain connectivity. Downward curvature is here associated with $\gamma < 0$, implying that $\Delta S_m > \Delta S_m^{id}$, which seems impossible if the ideal entropy is indeed the maximum. This is another reason for believing that negative curvature of $\chi_{NS}(\varphi)$ has causes other than thermodynamic ones (e.g., systematic errors).

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$$2\chi^{corr} = \frac{[1 - N_2\phi_2(\chi_{12} - \chi_{1v} + \chi_{2v})]^2}{N_2\phi_2[(2\chi_{2v} - f_s) - 1]}$$

With values appropriate for SANS experiments on isotope blends ($N\chi_{12} \approx 1$, $\chi_{1v} = \chi_{2v} \approx 2$, and $f_s = 1/\phi_v \approx 10$) the correction term χ^{corr} is of order χ_{12}/N and may safely be neglected.

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