

Zoller on the details of data acquisition. J. Dowell assisted with the three-dimensional plotting.

**Registry No.** Lexan 101 (SRU), 24936-68-3; Lexan 101 (homopolymer), 25037-45-0.

## References and Notes

- (1) Matheson, R. R. *Macromolecules*, preceding paper in this issue.
- (2) Theodorou, D.; Suter U. *Macromolecules* 1986, 19, 139.
- (3) Zoller, P.; Bolli, P.; Pahud, V.; Ackermann, H. *Rev. Sci. Instrum.* 1976, 47, 948.
- (4) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* 1982, 20, 1453.
- (5) Fisher, R. A.; Yates, F. *Statistical Table for Biological, Agricultural and Medical Research*, 6th ed.; Hofner: New York, 1963; pp 33-36, Table XXIII.
- (6) Nanda, V. S.; Simha, R. *J. Chem. Phys.* 1964, 41, 3870.
- (7) Crow, E. L.; Davis, F. A.; Maxfield, M. W. *Statistics Manual*; Dover: New York, 1960; pp 83-84.
- (8) Scott, A. H. *J. Res. Natl. Bur. Stand.* 1935, 14, 99.

## Excess Free Energies in Solutions of Isotopic Isomers. 3. Solutions of Deuteriated and Protiated Polymers

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*Received December 8, 1986*

**ABSTRACT:** Excess free energies and phase separation in mixtures of protio- and deuterio-substituted polymers are discussed in the context of the theory of isotope effects in condensed phases. In large molecules the internal degrees of freedom make the most important contributions to  $A^E$ , which is obtained by considering the volume dependence of the free energy and integrating over the concentration-weighted molar volume isotope effect but along a congruent path. Agreement with experiment is demonstrated for the poly(perprotio-1,4-butadiene)/poly(perdeuterio-1,4-butadiene) and poly(perprotiostyrene)/poly(perdeuteriostyrene) systems.

## Introduction

Recently Bates, Wignall, and Koehler<sup>1</sup> (BWK), Bates, Dierker, and Wignall,<sup>2</sup> and Bates and Wignall<sup>3</sup> (BW) made measurements of critical behavior and incipient phase separation in solutions of deuteriated and protiated polybutadiene<sup>1,2</sup> and of deuteriated and protiated polystyrene.<sup>3</sup> In related experiments Atkin et al.<sup>4</sup> and Yang et al.<sup>5</sup> have studied the effect of deuteration on phase separation in polymer blends. These studies owe their origin to questions arising in the interpretation of neutron diffraction studies of polymer blends and mixtures. Since the scattering intensity from neutrons and protons is so different, measurements of differential scattering cross sections from protio/deuterio solutions can be employed to answer questions concerning confirmation and shape, monomer-monomer pair distribution functions, chain tangling, etc.<sup>6</sup> The method is straightforward, however, only if the properties of the protio/deuterio solution are independent of isotopic label or if the isotope dependence is well understood in terms of the more fundamental potential energy surface (PES) describing the system. It is in this context that the experiments of Bates et al.<sup>1-3</sup> and others<sup>4,5</sup> are of interest. They unequivocally establish that substantial excess free energies exist in protio/deuterio solutions of polymers. Standard theories of solution<sup>7</sup> immediately lead to the prediction of phase separation of the upper consolute type. It is the purpose of this paper to demonstrate that this behavior is consistent with the theory of isotope effects in condensed phases<sup>8</sup> as recently applied by us to mixtures of isotopes.<sup>9</sup> The upper consolute solution temperatures (UCST's) calculated on the assumption of an isotope-independent PES are in good agreement with experiment. It is thus reasonable to assume that nonthermodynamic results, like neutron diffraction data, can also be interpreted with an isotope-independent PES. This is a useful and reassuring conclusion. In the present paper we restrict attention to solutions of isotopic isomers, one in the other.

## Excess Free Energies of Solutions of Isotopes

Singh and Van Hook<sup>9</sup> (SVH) have recently presented a theory of nonideality in solutions of isotopes. Following the lead of earlier authors including Prigogine, Bingen, and Bellemans,<sup>10</sup> Bigeleisen,<sup>11</sup> and Jancso and Van Hook,<sup>12</sup> they expanded the Helmholtz free energy about the respective equilibrium volumes of the separated samples. This time, however, a careful distinction between the contributions of intermolecular and intramolecular degrees of freedom was maintained. In the original Prigogine approach each separated isotope was compressed or dilated to the molar volume of the isotopic mixture and then mixed isochorically. The free energy of mixing was taken as the sum of the free energies of compression and dilation and of isochoric mixing (which was assumed to be zero). The result is a well-known expression relating the difference in molar volumes of the separated isotopes,  $\Delta V = V_1^0 - V_2^0$ , (subscript 1 refers to the lighter isotope), to the excess free energy of mixing

$$A^E = x_1 x_2 (\Delta V)^2 / (2\kappa V^0) \quad (1)$$

$\kappa$  is the isothermal compressibility. Equation 1 is presented in the approximation that neglects isotope effects on  $\kappa$  and  $V^0$  in the denominator. Buckingham and Hentschel<sup>13</sup> have presented an analysis that is similarly based.

We have criticized<sup>9</sup> the development leading to eq 1 on two counts. The first is on logical grounds. The theory of isotope effects assumes the PES's (appropriately expressed in reduced coordinates) are identical at the Born-Oppenheimer level for each of the separated isotopes and for the solutions formed from them. This straightforwardly leads to the conclusion that the distribution functions describing atom-atom correlations in the liquids, such as the two-particle correlation functions,  $n^2(r^*, \theta, \phi)$ , and the rotationally averaged radial distribution functions,  $g(r^*)$ , are also isotope independent. We use the term "congruent" to describe this situation. Here  $r^* = r/\sigma$  is a reduced distance, and  $\sigma$  is a length parameter specified

by the potential. Because it is well-known that the distribution functions  $n^2(r^*, \theta, \phi)$  and  $g(r^*)$  depend sensitively on density (and thus on pressure) SVH concluded that the very act of compressing a sample of the liquid substituted with one isotope and dilating a sample of the other before mixing them moves the two PES's away from congruency. In that event the isochoric mixing cannot occur at zero excess free energy, so eq 1 must be wrong. This conclusion is consistent with the observation that excess free energies obtained from eq 1 are not in agreement with experiment for isotopic mixtures of simple liquids.<sup>9</sup> A proper calculation of the relevant expansion or dilation must be carried out along a congruent path (i.e., at constant  $n^2(r^*, \theta, \phi)$  or  $g(r^*)$ ) and *not along the equilibrium thermodynamic path*. The volume difference that defines the end points of the congruent path is the one that arises from the quantum effect on the anharmonic isotope-independent intermolecular potential. SVH have presented a prescription to carry out a calculation of the free energy of mixing due to this effect.

Next we turn attention to the intramolecular degrees of freedom. These vibrations make important contributions to the isotopic difference in molar volumes and to the excess free energy of mixing. The molar volume isotope effect (MVIE) in polyatomics is largely accounted for by the observation that the mean amplitude of vibration is significantly larger for H than for D because the H isomer less higher in the well (PES). This results in an isotope effect on the core size.<sup>14-16</sup> Singh and Van Hook<sup>9</sup> considered the effect of intramolecular degrees of freedom by writing the partition function as a product of intermolecular and oscillator contributions,  $Q = Q(\text{intermolecular})Q(\text{oscillator})$ , where  $Q(\text{oscillator})$  is a  $3n$ -dimensional product of harmonic oscillator partition functions. At first glance this appears as if the contribution of the translational degrees of freedom has been considered twice but this is not so. The theory considers quantum effects on the intermolecular potential ( $Q(\text{intermolecular})$ ) and the isotope effect on the core size separately. Because of the large amplitude effects in hydro/deuteriocarbons the core effect predominates and is primarily responsible for the observed molar volume isotope effects.

To calculate the excess free energy of isotopic mixing the separated isotopes are *congruently compressed or dilated* to the molar volume of the solutions and then mixed isochorically. Thus, say for the light isotope

$$\mu_1^e/RT = \ln(\gamma_1) = - \int_{V_1^0}^V (d \ln Q(\text{intermol})/dV) dV - \int_{V_1^0}^{V^{3n}} (d \ln Q_i(\text{osc})/dV) dV \quad (2)$$

because  $\mu = -RT \ln Q$ . For large molecules at elevated temperatures, systems like the polymer mixtures considered in this paper, SVH have shown the contribution of the congruent intermolecular mixing is negligible compared to that from the second term.

### Polymer Mixtures

To apply the above formalism to an equimolar polymer solution of monodispersive isotopic isomers, we restrict the analysis to low pressure and consider the partial molar Helmholtz free energies,  $A_i = A_i^0(V_i^0) + \int_{V_i^0}^V (dA_i/dV) dV$ , so the free energy of the solution is

$$A_{\text{mix}} = x_1 A_1^0 + x_2 A_2^0 + x_1 \int_{V_1^0}^V (dA_1/dV) dV + x_2 \int_{V_2^0}^V (dA_2/dV) dV + RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (3)$$

The path integrals in eq 3 are understood to be congruent. For large massive molecules the external translational and librational modes are of ultralow frequency and make negligible contribution to  $A_{\text{mix}}$ . We assume the vibrational frequencies in the polymer can be factored into  $N$  sets of group frequencies,  $\nu_i$  ( $N$  the number of monomer units), and treat these in the pseudoharmonic approximation. Then<sup>9</sup>

$$\int_{V_i^0}^V (d(A_i/RT)/dV) dV = -N \int_{V_i^0}^{V^{3n}} \sum_i (d \ln Q_i/du_i)(du_i/dV) dV = -N \int_{V_i^0}^{V^{3n}} \sum_i u_i f(u_i) \gamma_i d \ln V \quad (4)$$

where  $\gamma_i = -d \ln u_i/d \ln V$ ,  $f(u_i) = (1/2 + \exp(-u_i)/(1 - \exp(-u_i)))$ , and  $u_i = h\nu_i/kT$ . For hydro/deuteriocarbons the CH/CD stretching frequencies make the predominant contribution to the isotope effect because they not only are the largest frequencies but also show the largest isotope sensitivity. Therefore following Jancso and Van Hook<sup>12</sup> we neglect bending and carbon skeletal modes.<sup>17</sup> For  $u_i > 2\pi$ ,  $f(u_i) = 1/2$  so

$$\int_{V_i^0}^V (dA_i/dV) dV = -N(RTr_i\gamma_i u_i/2) \ln(V/V_i^0) \quad (5)$$

Here  $r_i$  is the number of CH or CD stretching modes per monomer unit. Note  $r_{i,1} = r_{i,2}$ ,  $\gamma_1 = \gamma_2$  but  $u_1 \neq u_2$  and  $V_1^0 \neq V_2^0$ . Remember our notation represents the lighter isotope (H) as 1, the heavier (D) as 2.

We now return to eq 3 in the approximation of  $V^{\text{ex}} = 0$  for the isotopic mixture. In that case  $V = V_1^0 - x_2 \Delta V = V_2^0 + x_1 \Delta V$ ,  $\Delta V = V_1^0 - V_2^0$ , and  $\Delta V/V_1^0 \cong \Delta V/V_2^0 \cong \Delta V/V$ . Also  $\Delta V/V \ll 1$ , so

$$A/RT = x_1 A_1^0/RT + x_2 A_2^0/RT + x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 (N\gamma_i r_i/2)(\Delta V/V)(u_1 - u_2) \quad (6)$$

The conditions for phase separation are obtained by differentiating eq 6 with respect to concentration and setting the second and third derivatives equal to zero. In this way we find  $x_{1c} = x_{2c} = 0.5$  and

$$N_c(r_i\gamma_i/2)(\Delta V/V)u_i(1 - (\mu_1/\mu_2)^{1/2}) = 2 \quad (7)$$

The  $u_i$ 's are reduced masses for the CH or CD oscillators and should not be confused with the partial molar free energies,  $\mu_1/\mu_2 = (2^{-1} + 12^{-1})/(1^{-1} + 12^{-1})$ .

**Poly(propio/deuteriobutadiene).** For this material  $r_i = 6$ ,  $\Delta V/V = (4 \pm 1) \times 10^{-3}$ ,<sup>1</sup> and as for benzene<sup>9</sup> we take  $\gamma_i = 0.035$  and  $u_i = (1.44 \times 3000)/T = 14.4$  at 300 K, thereby deducing from eq 7 that  $N_c = (1.3 \pm 0.3) \times 10^3$ , in much better agreement with experiment ( $N_c = (2.3 \pm 0.5) \times 10^3$ )<sup>1</sup> than the result calculated by BWK<sup>1</sup> based on eq 1 ( $N_c = (6.6 \pm 3.1) \times 10^3$ ). The uncertainty in the present calculation reflects the experimental error reported by BWK for the  $\Delta V/V$  measurement. There is an additional uncertainty arising from error in the assignment of the Gruneisen coefficient. The results are summarized in Table I.

It is interesting to note that the estimate,  $N_c(300) = (1.3 \pm 0.3) \times 10^3$ , is probably a lower bound. This can be seen from the following argument. The application of regular solution theory in its simplest form (as above) to the phase separation problem leads to the prediction  $\beta = 0.5$  for the critical exponent in the relation

$$\Delta T_c = |x - x_c| = K((T_c - T)/T_c)^\beta = Kt^\beta \quad (8)$$

Close to  $T_c$  both theory and careful experiment have established a universal value,  $\beta = 0.325 \pm 0.003$ . In eq 8,  $K$

**Table I**  
Excess Free Energies in Two Protio/Deuterio Polymer Mixtures

material	T/K	10 <sup>4</sup> ln ( $\gamma_1^e$ )				
		expt	ref	this work	eq 1 and 14	eq 19
PB <sup>a</sup>	296	9 ± 2	1	13 ± 4 <sup>c</sup> 11 ± 4 <sup>d</sup>	4 ± 1	14
PS <sup>b</sup>	300	4 ± 2	3	7 ± 2 <sup>c</sup> 6 ± 2 <sup>d</sup>		10

<sup>a</sup> Poly(perprotio/perdeuteriobutadiene). <sup>b</sup> Poly(perprotio/perdeuteriostyrene). <sup>c</sup> 2/ $N_c$ ; see eqs 2 and 7. <sup>d</sup> Symmetrical approximation; see eq 12.

is a nonuniversal fitting parameter. The range of the nonclassical region for binary liquid mixtures (defined as the region where eq 8 with  $\beta = 0.325$  is universally expected to hold) has been recently discussed by Singh and Van Hook.<sup>18</sup> They conclude that nonclassical effects are substantially damped out in the range  $-4 < \log t < -3$ . Although for arbitrarily small values of DELTA any analytical representation of the free energy will lead classically to  $\beta = 0.5$  and a classical expression is not to be tolerated for  $\log(t)$  less than, say,  $-3.5$ , the authors<sup>18</sup> point out that eq 8 with  $\beta = 0.33 \pm 0.01$  empirically fits most binary liquid coexistence data of the UCST type over a wide range of  $t$ . That range sometimes extends to  $\log(t) = -0.7$  or further, i.e., 60 K or more below  $T_c$ , and thus far into the classical region. Furthermore the authors succeeded in representing the apparent  $\beta$  (now circumstantially in numerical agreement with the nonclassical value, 0.325, over the range  $10^{-3} < t < 2 \times 10^{-1}$ ) by a one-parameter mean-field treatment that follows the Guggenheim symmetrical mixture model.<sup>19</sup> Of course that model for small enough  $t$  will in the limit yield the classical exponent, 0.5, but this only happens at temperatures very close to  $T_c$ , temperatures inside the range of most data. The work of Binder<sup>20</sup> and Herkt-Maetzky and Schelton<sup>21</sup> indicates that polymer solutions and polymer melts switch over to a classical mean-field representation at even smaller values of  $t$ , and mean-field values have been reported for the exponents describing scattering correlation lengths and susceptibilities of polymer solutions.<sup>21</sup> Clearly, then, polymer solutions are classical in the mean-field sense, at least in the temperature range of interest to the present analysis. The question of present concern focuses on whether solutions of polymer isotopes are better represented as strictly regular solutions (giving an apparent  $\beta = 0.5$ ) or as symmetrical mixtures (with an apparent  $\beta < 0.5$  and even approaching 0.33). The available literature data, including BWK, are not sufficiently precise to resolve this question, which awaits refined measurements. The Singh-Van Hook analysis<sup>9,18</sup> establishes the symmetric mixture model as appropriate for a number of small-molecule liquid-liquid systems. These authors succeeded in quantitatively rationalizing both the phase diagrams and their pressure and isotope dependences with the symmetric model. Mixtures of polymer isotopomers are also reasonably assumed to be symmetric, and if so, higher order terms are required in the Redlich-Kister expression for  $A^e$ . For a given  $N_c$ , the effect is to broaden the two-phase region, lowering the predicted value of  $T_c$  (or equivalently raising  $N_c$ ) from the values given by the strictly regular calculation. It is that correction which is discussed in the next paragraph.

More specifically we write

$$V = V_1^0 - x_2\Delta V + V^e = V_2^0 + x_1\Delta V + V^e \quad (9)$$

and adopt the Redlich-Kister formalism for  $V^e$

$$V^e = x_1x_2(R_0 + R_1(1 - 2x_2) + R_2(1 - 2x_2)^2 + \dots) \quad (10)$$

Defining  $g_1 = Nr_1\gamma_1u_1/2$ ,  $g_2 = Nr_2\gamma_2u_2/2$  and  $\Delta g = g_1 - g_2$  gives (compare with eq 3 and 5)

$$A^e = x_1x_2((\Delta V/V)\Delta g + (g_1R_0/V) \times (1 - x_2\Delta g/g_1) + (g_1R_1/V)(1 - 2x_2)(1 - x_2\Delta g/g_1) + (g_1R_2/V)(1 - 2x_2)^2(1 - x_2\Delta g/g_1) + \dots) \quad (11)$$

For CH/CD substitution,  $\Delta g/g_1 = 0.266$ , and near  $x_c$   $x_2 = 0.5$  and  $(1 - x_2\Delta g/g_1) = 0.87$ . To obtain  $N_c$ , the expression for  $A(\text{total})$  is differentiated. If from symmetry we argue  $x_c = 0.5$ , which implies  $R_1 = 0$ , then the excess free energy is of the form

$$A^e = x_1x_2(M_0 + M_2(1 - 2x_2)^2) \quad (12)$$

with  $M_0 = ((\Delta V/V)\Delta g + 0.87g_1R_0/V)$  and  $M_2 = 0.87g_1R_2/V$ . At  $T_c$ ,  $(d^2A_{\text{mix}}/dx^2) = 0$ , so  $M_0 - M_2 = 2$ . For a regular solution  $H^e \cong G^e \cong A^e$  and  $S^e \cong 0$ . Arguments presented during the discussion on congruent compression indicate  $S^e \cong 0$  is a reasonable approximation for solutions of isotopes. In that case, with  $A^e$  represented by eq 12, the constraint  $\beta = 0.325$  implies  $M_2/M_0 = 0.2$ .<sup>18</sup> Since  $V^e/\Delta V \ll 1$  (i.e.,  $((\Delta V/V)(\Delta g)) \gg 0.87g_1R_0/V$ ), then  $(\Delta V/V)(\Delta g) = 2.4$ , which implies a 20% correction to  $N_c$  as calculated earlier. The corrected value becomes  $N_c(\text{calcd}) = (1.6 \pm 0.3) \times 10^3$ , which is within reach of the experimental value,  $N_c(\text{obsd}) = (2.3 \pm 0.5) \times 10^3$ . The uncertainties are those previously discussed plus any implied by the approximations in the evaluation of the correction. (Excess volumes in isotopic mixtures of polyatomics have been determined for the  $C_6H_6/C_6D_6$  system<sup>22</sup> near room temperature where the inequality  $V^e/\Delta V \ll 1$  is obeyed.)

**Poly(protio/deuteriostyrene).** Bates and Wignall<sup>23</sup> report  $N_c(300) = (3.8 \pm 0.8) \times 10^3$ . Application of eq 7 is not straightforward. To begin with we estimate the molar volume isotope effect of polystyrene (which has not been measured) as the average of that for benzene/deuterio-benzene in the low-temperature approximation ( $2 \times 10^{-3}$ ) and a skeletal CH/CD effect which we take as half that for polybutadiene (three vs. six skeletal hydrogens), also  $2 \times 10^{-3}$ . When the uncertainty is set equal to that for polybutadiene (one in four),  $\Delta V/V = (2 \pm 0.5) \times 10^{-3}$ . With  $\gamma_{CH} = 0.035$  (see above) and  $r_i = 8$ , eq 7 gives  $N_c(300) = (2.7 \pm 0.7) \times 10^3$ . The error limit reflects only the uncertainty in the value assigned to the MVIE. Correction to the symmetric model (see above) will raise  $N_c(300)$  to about  $3.2 \times 10^3$ , in better agreement with the experimental value. It is unfortunate that the experimental conditions for the polystyrene measurements (i.e., annealing at elevated temperature) and the absence of MVIE data make it impossible to define the parameters of the theory more closely and thus preclude a more direct test, i.e., one at the experimental temperature. (Our present theoretical understanding of the temperature dependence of MVIE's<sup>16,24</sup> is not sufficient to permit this parameter to be accurately estimated at the rather high experimental temperatures of ref 3, nor are any Gruneisen constants available there.)

#### Interpretation of Bates and Wignall: The Polarizability Isotope Effect

Late in 1986 Bates and Wignall<sup>23</sup> presented an interpretation of their data<sup>1-3</sup> different from the one developed above. They decomposed the parameter describing the excess free energy of interaction into two parts, writing the equivalent of

$$A^e/RT = x_1x_2(\chi_v + \chi_d) \quad (13)$$

(Actually BW employ volume rather than mole fraction

statistics, but for the polymer solutions of interest to us the two are equivalent.) By following an analysis like that leading to eq 1, they obtain

$$\chi_v = (\Delta V)^2 / (2\kappa V) \quad (14)$$

We have criticized this result above and in ref 18. It is the end product of an integration of a volume-dependent free energy over the molar volume isotope effect (primarily determined by amplitude isotope effects of the CH stretching motions), but along a noncongruent path. The relative contribution of the inter- and intramolecular degrees of freedom are left unspecified. The compressibility is related to the low-frequency chain distortion and intermolecular modes, both of which show a relatively small isotope dependence. The more important contributions from internal modes with significant isotope dependence are not included in equations like (14), even if the path of integration be changed to a congruent one. BW recognized the inadequacy of eq 14 and introduced the  $\chi_d$  parameter to "account for the difference in ... van der Waals forces between deuteriated and protonated polymers".

$\chi_d$  can be estimated by combining the Flory-Huggins definition

$$kT\chi_d = (\epsilon_{HD} - (\epsilon_{HH} + \epsilon_{DD})/2) \quad (15)$$

with the London formula for the dispersion energy<sup>25</sup>

$$S^6\epsilon_{AB} = -(3/2)(I_A I_B / (I_A + I_B))\alpha_A \alpha_B + \text{vibrational correction terms} \quad (16)$$

Here  $\epsilon$  is the segment-pair interaction energy,  $\alpha$  the polarizability,  $k$  the Boltzmann constant,  $I$  the ionization potential, and  $S$  a distance parameter. The vibrational correction terms, VCT, introduced by Wolfsberg<sup>26</sup> are conveniently expressed in terms of sums over the absolute intensities,  $\Gamma_i$ , of the  $i$  normal mode frequencies.<sup>25-30</sup>

$$\text{VCT} = -(3hc/(4N_{av}\pi^3))[\sum_i \Gamma_{i,A}\alpha_B + \sum_i \Gamma_{i,B}\alpha_A] \quad (17)$$

Writing  $I_D = I_H(1 - \Delta I/I)$ ,  $\alpha_D = \alpha_H(1 - \Delta\alpha/\alpha)$ ,  $W_H = [3hc/(4N_{av}\pi^3)\sum_i T_{i,H}]$ ,  $W_D = [3hc/(4N_{av}\pi^3)\sum_i \Gamma_{i,D}]$ ,  $W_D = W_H(1 - \Delta W/W)$  and making the indicated substitutions, we obtain thru second order in the differential quantities

$$S^6 kT\chi_d = (3/8)I\alpha^2[(\Delta\alpha/\alpha)^2 + (\Delta\alpha/\alpha)(\Delta I/I)] + \alpha_H W_H(\Delta\alpha/\alpha)(\Delta W/W) \quad (18)$$

The cross product,  $(\Delta I/I)(\Delta\alpha/\alpha)$ , is certainly much smaller than  $(\Delta\alpha/\alpha)^2$ , so eq 18 simplifies<sup>31</sup>

$$S^6 kT\chi_d = (\Delta\alpha/\alpha)[(3/8)I\alpha^2(\Delta\alpha/\alpha) + \alpha_H W_H(\Delta W/W)] \quad (19)$$

If the second term on the right is dropped from eq 19 the result is equivalent to the one of BW, which they obtained less generally by assuming  $I$  to be isotope independent. That assumption is not necessary because the excess free energy of mixing of isotopes is a second-order effect and enters only as a square or cross product of first-order isotope effects.

The isotope effect on  $W$  is given in terms of a well-established isotope sum rule,<sup>28,29</sup> and intensities are available for simple molecules. For methane/perdeuteriomethane the second term only amounts to about 3% of the first and at the present level of precision can be ignored. However, for larger molecules (segments) the integrated intensities are larger. Also according to the data tabulated by Rabinovich,<sup>32</sup>  $(\Delta\alpha/\alpha)$  may be smaller. The intensity ratio of the perprotio and perdeuterio species will remain roughly the same so the relative contribution of the second term

increases. For example, for the  $C_6H_6/C_6D_6$  system, which is of interest for the interpretation of the polystyrene data above,  $(\Delta\alpha/\alpha) = 0.005$ , about one-third of the value for methane, and the second term in eq 19 is about three-tenths of the first.<sup>33</sup> Clearly it can no longer be ignored. One expects the vibrational correction term to be important in many cases.

In eq 17-19 excess free energy is rationalized in terms of the isotope effect on polarizability. The difference in polarizability derives from the slightly more extended electron distribution in the protiated as compared to the deuteriated molecule. Just like the MVIE, the polarizability isotope effect is to be understood in terms of an isotope-independent PES describing the intramolecular vibrations. The two effects share a common origin. Wolfsberg<sup>26</sup> has considered isotope effects on condensed-phase free energies. He demonstrated the equivalence of an explanation based on the London formula as originally suggested by Baertschi and Kuhn<sup>34</sup> (i.e., a development similar to that of BW, or the one above) and the more conventional formalism of Bigeleisen and others<sup>8</sup> expressed in terms of the force constant changes in an isotope-independent PES which occur on the transfer from the standard state. This is just the situation that obtains here. In the approach used in the first part of this paper the relevant force constant shifts are related to the MVIE using a Gruneisen theory. The Baertschi-Kuhn, Bates-Wignall formalism instead uses information on the polarizability isotope effect and assumptions about the nature of the repulsive part of the potential (to evaluate  $S^6$ ). Fang and Van Hook<sup>27</sup> have previously discussed the relationships between the MVIE,  $(\Delta\alpha/\alpha)$ , effective van der Waals forces, and the PES in yet another context. In any case, the important point is that fundamentally the two approaches are equivalent. However several important cautions remain. (1) Discussion of the calculation of isotope effects on effective van der Waals energies often fails to emphasize the essential isotope independence of the PES defining the process. (2) Experimental values of the parameters used in the vdW approach ( $(\Delta\alpha/\alpha)$  and  $S$ ) are not as well established as the spectroscopic and MVIE parameters employed in the alternate approach. Also, vibrational corrections to the effective van der Waals energies may be difficult to evaluate.

Bell<sup>35</sup> and Frivold, Hassel, and Hetland<sup>36</sup> report the polarizability of CH to be about 1.4% larger than CD for methane. Rabinovich<sup>32</sup> reports refractive index measurements on a variety of CHO compounds and interprets them in terms of polarizability effects varying between 0.1 to slightly more than 1% or so but always with  $\alpha_H > \alpha_D$ . Scher, Ravid, and Halevi<sup>37</sup> made high-precision measurements of the polarizability H/D isotope effects in HCl and NH<sub>3</sub>, demonstrating that the earlier values reported by Bell<sup>35</sup> and Bell and Coop<sup>38</sup> for these compounds were high. Thus, although it is clear that  $(\Delta\alpha/\alpha)$  is positive, significant uncertainty remains in the numerical values of the effect. It is left to insert an estimate for  $S^6$  in eq 15. This BW do by accepting the rough approximation that  $S$  can be equated to the hard-sphere segment radius,  $S = (3V/4\pi)^{1/3}$ ,  $V$  is the volume per segment. The estimates of the conditions for critical phase separation from eq 19 are compared with the ones obtained in the first part of this paper and with experiment in Table I.

## Conclusion

Nonideality in mixtures of isotopic isomers of polymers has been shown to be a natural consequence of the dynamics of atomic motion on the isotope-independent potential surface describing the condensed phase. Important

contributions arise from the internal degrees of freedom. We have shown that it is profitable to consider the excess free energy of the mixture as a function of the isotope effect on the molar volume. It is to be emphasized that differential compression (or dilation) over the isotopic volume difference must be carried along a congruent path and not along the one defined by the equilibrium thermodynamic isothermal compressibility. The result is an important one because it should allow one to establish a prescription so that the dynamics of polymer motion in H/D mixtures can be used to explore the nature of the PES using neutron diffraction or other investigations. Finally it was demonstrated that the present method of calculation is equivalent to one expressed in terms of effective van der Waals forces but has advantages over that formalism.

**Acknowledgment.** This work was sponsored by the National Science Foundation under Grant CHE-84-13566.

**Registry No.** Polybutadiene, 9003-17-2; poly(perdeuteriobutadiene), 29989-19-3; polystyrene, 9003-53-6; poly(perdeuteriostyrene), 27732-42-9.

## References and Notes

- (1) Bates, F. S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev. Lett.* **1985**, *55*, 2425.
- (2) Bates, F. S.; Dierker, S. B.; Wignall, G. D. *Macromolecules* **1986**, *19*, 1938.
- (3) Bates, F. S.; Wignall, G. D. *Macromolecules* **1986**, *19*, 932.
- (4) Atkin, E. L.; Kleintjens, L. A.; Koningsveld, R.; Fetters, L. J. *Makromol. Chem.* **1984**, *185*, 377.
- (5) Yang, H.; Shibayama, M.; Stein, R. S.; Shimizu, N.; Hashimoto, T. *Macromolecules* **1986**, *19*, 1667.
- (6) Olabisi, Q.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979. Fischer, E. W. *IUPAC 27th Int. Symp Macromol.* **1981** *1982*, 191. Walsh, D. J.; Higgins, J. S.; Maconnachie, A. *Polymer Blends and Mixtures*; Martinus Nijhoff: Dordrecht, 1985; NATO ASI Ser.
- (7) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY 1953. Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440; *J. Phys. Chem.* **1942**, *46*, 151. Hildebrand, J. H.; Scott, R. L. *The solubility of nonelectrolytes*; Reinhold: New York, 1950.
- (8) Bigeleisen, J. *J. Chem. Phys.* **1961**, *34*, 1485. Jancso, G.; Van Hook, W. A. *Chem. Rev.* **1974**, *74*, 689.
- (9) Singh, R. R.; Van Hook, W. A. *J. Chem. Phys.* **1987**, *86*, 2969.
- (10) Prigogine, I. *The molecular theory of solutions*; North-Holland: Amsterdam, 1957. Prigogine, I.; Bingen, R.; Bellemans, A. *Physica* **1954**, *20*, 633.
- (11) Bigeleisen, J. *J. Chem. Phys.* **1963**, *39*, 769.
- (12) Jancso, G.; Van Hook, W. A. *Physica* **1978**, *91A*, 619.
- (13) Buckingham, A. D.; Hentschel, H. G. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 853.
- (14) Bartell, L. S.; Roskos, R. R. *J. Chem. Phys.* **1966**, *44*, 457.
- (15) Menes, F.; Dorfmueller, T.; Bigeleisen, J. *J. Chem. Phys.* **1970**, *53*, 2869.
- (16) Van Hook, W. A. *J. Chem. Phys.* **1985**, *83*, 4107.
- (17) The isotope dependence of these modes can be calculated by standard methods. (Siesler, H. W.; Holland-Moritz, K. *Infrared and Raman Spectroscopy of Polymers*; Marcel Dekker: New York, 1980.) However their relative contribution is small. For low frequencies, like the skeletal modes,  $u_f(u_i)$  approaches unity, so for an isotope-independent Gruneisen coefficient these modes do not contribute to the isotope effect. Intermediate modes, like the bends, do show some isotope sensitivity in  $u_f(u_i)$  but much less than the CH/CD stretches. Moreover  $\gamma_i$  for these frequencies is small.
- (18) Singh, R. R.; Van Hook, W. A. *J. Chem. Phys.*, in press.
- (19) Guggenheim, E. A. *Applications of Statistical Mechanics*; Clarendon: Oxford 1966.
- (20) Binder, K. *Phys. Rev. A* **1984**, *29*, 341.
- (21) Herkt-Maetzky, C.; Schelton, J. *Phys. Rev. Lett.* **1983**, *51*, 896.
- (22) Dutta-Choudhury, M. K.; Dessauges, G.; Van Hook, W. A. *J. Phys. Chem.* **1982**, *86*, 4068.
- (23) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
- (24) Koener, Z. S.; Van Hook, W. A. *J. Phys. Chem.* **1986**, *90*, 4860.
- (25) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
- (26) Wolfsberg, M. *J. Chim. Phys. Physicochim. Biol.* **1963**, *60*, 15.
- (27) Fang, A.; Van Hook, W. A. *J. Chem. Phys.* **1974**, *60*, 3513.
- (28) Overend, J. *IR Spectroscopy and Molecular Structure*; Elsevier: New York, 1963.
- (29) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular vibrations*; McGraw-Hill: New York, 1955.
- (30) Sverdlov, L. M. *Opt. Spectrosc.* **1962**, *12*, 66.
- (31) To estimate this, consider methane as an example. In the ground state the isotope effect on vibrational energy per CH stretch is about  $800\text{ cm}^{-1}$ . The ionization energy is on the order of 10 eV. Even if we assume complete vibrational relaxation in the excited (ionized) state, which is unreasonable,  $\Delta I/I$  will still lie significantly below  $10^{-3}$ . A more realistic estimate sets it well below  $5 \times 10^{-4}$ . Since  $\Delta\alpha/\alpha$  is on the order of  $10^{-2}$ ,  $(\Delta\alpha/\alpha)(\Delta I/I) \ll (\Delta\alpha/\alpha)^2$ .
- (32) Rabinovich, I. B. *Influence of Isotropy on the Physicochemical Properties of Liquids*; Consultants Bureau: New York, 1970.
- (33) Zelano, A. J.; King, W. T. *J. Chem. Phys.* **1970**, *53*, 4444.
- (34) Baertschi, P.; Kuhn, W. *Helv. Chim. Acta* **1957**, *40*, 1084.
- (35) Bell, R. P. *Trans. Faraday Soc.* **1942**, *38*, 422.
- (36) von Frivold, O. E.; Hassel, O.; Hetland, E. *Phys. Z.* **1939**, *40*, 29.
- (37) Scher, C.; Ravid, B.; Halevi, E. A. *J. Phys. Chem.* **1982**, *86*, 654.
- (38) Bell, R. P.; Coop, I. *Trans. Faraday Soc.* **1983**, *34*, 1209.