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Pressure dependence of the miscibility of poly(vinyl methyl ether) and polystyrene: Theoretical representation

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The present calculations were performed on the basis of the Sanchez-Lacombe-Balasz lattice fluid theory. The two system specific parameters ε_{12}^* and $\delta\varepsilon^*$ required for that purpose have been obtained from the spinodal temperatures measured (SANS) for mixtures of poly(vinyl methyl ether) (PVME) and deuterated polystyrenes (*d*-PS) by Schwahn and coworkers. The experimental data reported for atmospheric pressure and six representatives of the present system are well described theoretically, where ε_{12}^* does not depend on molar mass and $\delta\varepsilon^*$ decreases only slightly as the chain length of *d*-PS is raised. The measured pressure influences on the spinodal conditions correspond to an approximately linear reduction of $\delta\varepsilon^*$ with increasing *P*; this observation should reflect the volume changes associated with the formation of specific interactions. According to the present calculations the critical composition shifts markedly towards pure PVME as *P* is raised. Since experimental data are commonly expressed in terms of the Flory-Huggins theory, the current results were also translated into Flory-Huggins interaction parameters and evaluated with respect to the contributions of enthalpy and of entropy. The agreement between experimental information and that calculated from the Sanchez-Lacombe-Balasz lattice fluid theory is reasonable. © 1997 American Institute of Physics. [S0021-9606(97)51431-0]

I. INTRODUCTION

The first analytical description of the energy of mixing for polymeric systems was given by Flory¹ and Huggins.² This approach does not explicitly take into account the effects of expansion or compression due to a variation of temperature or pressure. The theory splits the energy of mixing into a combinatorial part and a residual part, where the latter defines the interaction parameter *g*. However, already 1942 Flory³ mentioned that the lattice of a molten polymer “will contain a few vacant cells” and “these vacant cells should be treated as molecules of a second component.” The incorporation of such free volume-effects lead to the theories based on equations of state like that of Flory, Orwoll and Vrij⁴ or Sanchez and Lacombe,^{5,6} later extended by Sanchez and Balasz.⁷ These theories can be used to calculate the temperature and pressure dependence of *g*. Such computations and the separation of *g* into its enthalpic and entropic contributions, *g_H* and *g_S*, have been reported for instance by Flory and Höcker⁸ for the former approach, for the latter by Sanchez and Lacombe.⁹

In the present paper we report on the calculation of spinodal curves for blends of poly (vinyl methyl ether) and polystyrene (PVME/PS) at different pressures. This computation is based on the Sanchez-Lacombe-Balasz lattice fluid theory and on parameters which are determined by adjusting the calculated spinodals to spinodal temperatures detected by

small angle neutron scattering at various pressures. The entropic and enthalpic parts of the interaction parameter are calculated and compared with experimental data.

II. THEORETICAL BACKGROUND

A. Flory-Huggins theory

Basis of the Flory-Huggins lattice model^{1,2} is the division of the entire system into lattice sites of equal size, where the magnitude of this reference volume *V_r* can be chosen arbitrarily. The theory disregards any effects of expansion by changes in pressure or temperature since the reference volume, once fixed, does not vary with *P* or *T*. The molecules of each component *i* are then treated as chains of *N_i* segments, where each segment occupies one lattice site, i.e. *N_i* is calculated by dividing the molecular volume *V_i* by *V_r*. Distributing these chains onto the lattice gives access to the Gibbs energy of mixing

$$\frac{\Delta G_M^{FH}}{kTV} = \frac{\varphi_1}{V_1} \ln \varphi_1 + \frac{\varphi_2}{V_2} \ln \varphi_2 + \frac{g}{V_r} \varphi_1 \varphi_2, \quad (1)$$

where *V* is the total volume of binary polymer system, φ_i the volume fraction of component *i*, and *k* the Boltzmann constant. The last term in Eq. (1) accounts for deviations from the ideal combinatorial entropic part. It contains the Flory-Huggins interaction parameter *g* describing the interaction between a segment of component 1 with one of 2. Since *g* depends on the size of the segment, we only deal with the quotient *g/V_r* which is independent on *V_r*.

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$$\gamma = \frac{g}{V_r} = \frac{\Delta G_M^{FH}}{kTV} - \left(\frac{\varphi_1}{V_1} \ln \varphi_1 + \frac{\varphi_2}{V_2} \ln \varphi_2 \right). \quad (2)$$

The Flory-Huggins interaction parameter was divided into the enthalpic and entropic parts as reported in the literature.¹⁰ It must be kept in mind that γ_h and γ_s are not defined as usual^{8,9} where g is the sum of g_H and g_S , i.e. g_H corresponds to γ_h/T and g_S to $-\gamma_s$

$$\gamma = \frac{\gamma_h}{T} - \gamma_s. \quad (3)$$

It turned out that the concentration dependence of these two parameters is often well described by first order polynomials

$$\gamma_h = A \varphi_{d-PS} + B, \quad \gamma_s = (C \varphi_{d-PS} + D) \cdot 10^{-3}. \quad (4)$$

The above equations are already formulated for PVME/*d*-PS, the polymer blend of present interest; φ_{d-PS} is the volume fraction of *d*-PS.

The interaction parameter¹¹ resulting from scattering experiments like SANS is not identical with the g value defined by Eq. (1), but constitutes a different interaction parameter called Γ . According to Eq. (5) of Ref. 10 the following relation with γ holds true

$$\Gamma = \gamma - (1 - 2\varphi_{d-PS}) \frac{\partial \gamma}{\partial \varphi_{d-PS}} - \frac{1}{2} \varphi_{d-PS} (1 - \varphi_{d-PS}) \frac{\partial^2 \gamma}{\partial \varphi_{d-PS}^2}. \quad (5)$$

Γ can be split into its enthalpic and entropic contributions, analogously to γ ,

$$\Gamma = \frac{\Gamma_h}{T} - \Gamma_s, \quad (6)$$

$$\begin{aligned} \Gamma_h &= \gamma_h - (1 - 2\varphi_{d-PS}) \frac{\partial \gamma_h}{\partial \varphi_{d-PS}} \\ &\quad - \frac{1}{2} \varphi_{d-PS} (1 - \varphi_{d-PS}) \frac{\partial^2 \gamma_h}{\partial \varphi_{d-PS}^2} \\ &= (3\varphi_{d-PS} - 1)A + B, \end{aligned} \quad (7)$$

$$\begin{aligned} \Gamma_s &= \left[\gamma_s - (12\varphi_{d-PS}) \frac{\partial \gamma_s}{\partial \varphi_{d-PS}} - \frac{1}{2} \varphi_{d-PS} (1 - \varphi_{d-PS}) \frac{\partial^2 \gamma_s}{\partial \varphi_{d-PS}^2} \right] \\ &= [(3\varphi_{d-PS} - 1)C + D] \cdot 10^{-3}. \end{aligned} \quad (8)$$

B. Sanchez-Lacombe-Balasz lattice fluid (SLB) theory

The starting point of the Sanchez-Lacombe lattice fluid model^{5,6} (SL) and its extension⁷ (SLB) is very similar to that of the previous approach, the novelty is the introduction of empty sites allowing the system to expand or shrink as P or T are varied. In the close-packed state all sites are occupied and the system has reached its maximum density. Since the close-packed volume of mixing is zero, a new, more convenient concentration variable is introduced, the close-packed volume fraction ϕ_i . In the nomenclature of Sanchez-Lacombe the number of segments per molecule is r and the

number of molecules is N . The Gibbs energy of mixing is related to the Gibbs energy per mer (indicated by the double bar) of the mixture (index M) and that of the components (index 1 or 2) by

$$\Delta G_M^{SLB} = rN[\bar{G}_M^{SLB} - (\phi_1 \bar{G}_1^{SLB} + \phi_2 \bar{G}_2^{SLB})]. \quad (9)$$

The Gibbs energy of a pure component per mer reads

$$\begin{aligned} \bar{G}_i &= \varepsilon_{ii}^* \left\{ \bar{\rho}_i + \bar{P}_i \bar{v}_i + \bar{T}_i \left[(\bar{v}_i - 1) \ln(1 - \bar{\rho}_i) \right. \right. \\ &\quad \left. \left. + \frac{1}{r_i^0} \ln \left(\frac{\bar{\rho}_i}{\omega_i^0} \right) \right] \right\} \end{aligned} \quad (10)$$

and of the mixture

$$\begin{aligned} \bar{G}_M &= \varepsilon^* \left\{ -\bar{\rho} + \bar{P} \bar{v} + \bar{T} \left[(\bar{v} - 1) \ln(1 - \bar{\rho}) + \frac{1}{r} \ln \bar{\rho} \right. \right. \\ &\quad \left. \left. + \frac{\phi_1}{r_1} \ln \frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2} \ln \frac{\phi_2}{\omega_2} \right] \right\}, \end{aligned} \quad (11)$$

r , the average number of lattice sites occupied by a molecule in the mixtures is related to the values of the components r_i by

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2}. \quad (12)$$

The volume of one lattice site v^* cannot be chosen arbitrarily in the SL model, as will be described later, and is unlike for the mixture and for the pure components (indicated by the superscript 0). In other words, the number of mers of a certain component is not identical in the mixture and in the pure state, i.e. r_i differs from r_i^0 .

ω_i and ω_i^0 are the number of configurations available to a r_i -mer and r_i^0 -mer in the close-packed state.^{5,12} This number is experimentally inaccessible, only its maximum value can be deduced by means of statistical considerations. Sanchez and Lacombe^{5,6} assumed that all ω_i are independent of composition and can thus be neglected in the equations for the Gibbs energy of mixing. In the present paper ω_i is set equal to the maximum possible value and so this parameter becomes composition dependent,

$$\omega_i = \delta_i r_i / \sigma_i e^{r_i - 1}, \quad \omega_i^0 = \delta_i^0 r_i^0 / \sigma_i^0 e^{r_i^0 - 1}, \quad (13)$$

with δ_i and δ_i^0 , the flexibility parameter of an r_i -mer and r_i^0 -mer, given by

$$\delta_i = \delta_{i,\max} = z(z-1)^{r_i-1}, \quad \delta_i^0 = \delta_{i,\max}^0 = z(z-1)^{r_i^0-1}, \quad (14)$$

where z is the coordination number of the lattice and σ_i plus σ_i^0 are the symmetry numbers of an r_i -mer and r_i^0 -mer ($\sigma_i = \sigma_i^0 = 1$ in the present case); $\bar{\rho}_i$, \bar{P}_i , \bar{v}_i , \bar{T}_i and $\bar{\rho}$, \bar{P} , \bar{v} , \bar{T} are the reduced density, pressure, volume, and temperature of the pure component i and of the mixtures, respectively; they are calculated by dividing them by the corresponding reduction parameter,

$$\tilde{X} = \frac{X}{X^*}, \quad X = P, v, T, P_i, v_i, T_i. \quad (15)$$

The reduced density gives the fraction of occupied sites, and is the inverse of the reduced volume,

$$\tilde{\rho} = 1/\tilde{v}, \quad \tilde{\rho}_i = 1/\tilde{v}_i. \quad (16)$$

The single reduction parameters are interrelated by ε^* the total interaction energy per mer, respectively. These equations also fix the value of v^* ,

$$P^* = \varepsilon^*/v^*, \quad P_i^* = \varepsilon_{ii}^* \varepsilon_{ii}^*/v_i^*, \quad (17)$$

$$T^* = \varepsilon^*/k, \quad T_i^* = \varepsilon_{ii}^*/k. \quad (18)$$

The scaling parameters T^* , P^* , and ρ^* can be calculated by fitting the following equation of state to PVT data,

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0. \quad (19)$$

For the pure component r is equal to r_i^0 which can be calculated from the reduction parameters for the pure components and the molecular Mass M_i

$$r_i^0 = \frac{M_i P_i^*}{k T_i^* \rho_i^*}. \quad (20)$$

The scaling parameters of the mixture are related to those of the pure components. The size of one lattice site in the mixture, v^* , and in the pure component i , v_i^* , have to fulfill the condition, that the close packed volume of one molecule is the same in the mixture and in the pure state,

$$r_i v^* = r_i^0 v_i^*. \quad (21)$$

The inverse of the mer size exhibits a linear dependence on the composition variable ϕ as can be deduced from the above equations,

$$\frac{1}{v^*} = \frac{\phi_1}{v_1^*} + \frac{\phi_2}{v_2^*}. \quad (22)$$

The entire close-packed volume of the systems reads

$$V^* = (r_1 N_1 + r_2 N_2) v^* \quad (23)$$

and the entire volume

$$V = r N v^* \tilde{v}. \quad (24)$$

For the pure component i there are only interactions between i and i so that ε^* is identical to ε_{ii}^* , the interaction energy for an i - i contact. In a binary mixture there are three possible contacts: 1-1, 2-2, and 1-2. Therefore ε^* consists of the three interaction energies scaled by the probability for the specific contact. ε_{ij}^* is the interaction energy of a mer belonging to component i when it is surrounded by z mers belonging to component j

$$\varepsilon^* = \phi_1^2 \varepsilon_{11}^* + 2 \phi_1 \phi_2 \varepsilon_{12}^* + \phi_2^2 \varepsilon_{22}^*. \quad (25)$$

For the generalized lattice fluid theory by Sanchez and Balasz (SLB),⁷ the 1-2 interaction becomes temperature dependent by introducing two types of 1-2 interaction: a weak (nonspecific) characterized by ε_{12}^* and a strong (specific) by $\varepsilon_{12}^* + \delta\varepsilon^*$. ε^* then reads

$$\varepsilon^* = \phi_1^2 \varepsilon_{11}^* + 2 \phi_1 \phi_2 f_{12}^* + \phi_2^2 \varepsilon_{22}^* \quad (26)$$

with

$$f_{12}^* = \varepsilon_{12}^* + \delta\varepsilon^* \frac{z k T}{2} \ln \left[\frac{1+q}{1+q \exp(-2 \delta\varepsilon^*/z k T)} \right], \quad (27)$$

where q is the ratio of the statistical degeneracies of the nonspecific and specific interaction states. In the present calculation z is set 12, and q 10. If $\delta\varepsilon = 0$, the SLB reduces to SL. ε_{12}^* and $\delta\varepsilon^*$ can be obtained by fitting calculated spinodal or binodal curves to experimental data. The spinodal and binodal are calculated by a method^{13,14} not requiring the derivatives of the Gibbs energy developed recently.

TABLE I. Scaling parameters and molecular weights.

	T_i^*, K	$P_i^*, \text{ atm}$	$\rho_i^*, \text{ g/cm}^3$
PVME ^a	657	3580	1.10
d -PS ^b	715	3526	1.192
	$M_w/\text{g/mol}$	M_w/M_n	$10^{-3} \cdot r_i^0$
PVME 89 ^c	89 000	2.5	5338.6
PVME 64.3 ^{d,e}	64 300	1.98	3857.0
d -PS 78.5 ^c	78 502	1.05	3932.6
d -PS 232 ^{c,d}	231 990	1.08	11622
d -PS 379 ^d	379 000	1.97	18987
d -PS 783 ^d	783 000	1.33	39226
d -PS 983 ^e	983 000	...	49246

^aFrom Ref. 7.

^bThe scaling parameters are obtained by fitting the equation of state, Eq. (19), with the PVT data (Ref. 18) for PS and the temperature and pressure are from 100 to 250 °C and from 1 to 1500 bar, respectively. The scaling density is calculated by the correction of 112/104 applied to account for deuteration of PS.

^cReference 15.

^dReference 16.

^eReference 10.

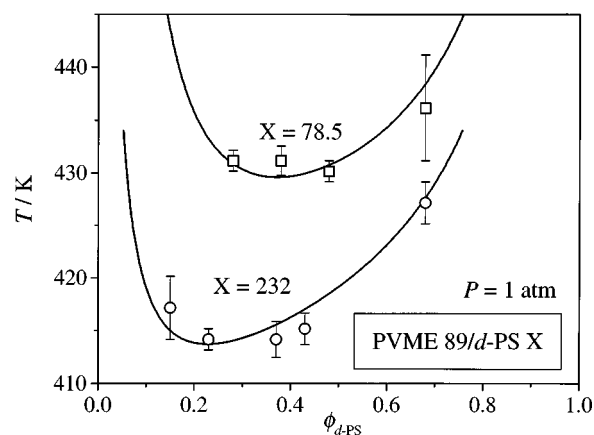


FIG. 1. Spinodal temperatures determined by small angle neutron scattering (Ref. 15) (SANS, open symbols) and calculated spinodals (solid lines) with $\varepsilon_{12}^* = 657$ K and $\delta\varepsilon^* = 305.26$ K for the blend poly(vinyl methyl ether) 89/deuterated polystyrene 78.5 (PVME 89/PS 78.5, the figures in this abbreviation indicate the molar mass in kg/mol) and $\delta\varepsilon^* = 304.80$ K for PVME 89/PS 232.

C. Expression of the Flory-Huggins interaction parameter in terms of the SLB theory

One of the topics of this paper is the calculation of the interaction parameter of the Flory-Huggins model by means of the SLB theory. Starting point is the consideration that the Gibbs energy of mixing ΔG_M^{real} is a property of the system and must not depend on the theoretical model chosen for its description,

$$\Delta G_M^{\text{real}} = \Delta G_M^{\text{FH}} = \Delta G_M^{\text{SLB}}. \quad (28)$$

In order to calculate g , ΔG_M^{FH} in Eq. (2) is replaced by ΔG_M^{SLB} of Eq. (9). A difficulty lies in the calculation of the

volume fraction φ_i . If we assume that the free volume, i.e. the volume of the vacancies, is distributed among the different components corresponding to their closepacked volume fraction, the volume that is occupied by component i is $r_i v^* \tilde{v}$. This argumentation leads to the equality of volume fraction and the close-packed volume fraction,

$$\varphi_i = \phi_i. \quad (29)$$

Equation (2) can then be rewritten on the basis of the SLB theory as

$$\gamma = \frac{1}{(v^* \tilde{v}) \phi_1 \phi_2} \left\{ \begin{aligned} & \frac{-\tilde{\rho} + \tilde{P} \tilde{v}}{\tilde{T}} - \left[\phi_1 \frac{-\tilde{\rho}_1 + \tilde{P}_1 \tilde{v}_1}{\tilde{T}_1} + \phi_2 \frac{-\tilde{\rho}_2 + \tilde{P}_2 \tilde{v}_2}{\tilde{T}_2} \right] + (\tilde{v} - 1) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} \\ & - \left[\phi_1 \left((\tilde{v}_1 - 1) \ln(1 - \tilde{\rho}_1) + \frac{1}{r_1^0} \ln \tilde{\rho}_1 \right) + \phi_2 \left((\tilde{v}_2 - 1) \ln(1 - \tilde{\rho}_2) + \frac{1}{r_2^0} \ln \tilde{\rho}_2 \right) \right] \\ & + \phi_1 \left(\frac{1}{r_1^0} \ln \omega_1^0 - \frac{1}{r_1} \ln \omega_1 \right) + \phi_2 \left(\frac{1}{r_2^0} \ln \omega_2^0 - \frac{1}{r_2} \ln \omega_2 \right) \end{aligned} \right\}. \quad (30)$$

The above relation can be rationalized as follows: In the case of the FH lattice the reference volume of one lattice site can be arbitrarily chosen and, comparing Eqs. (2) and (30), an appropriate value seems to be $v^* \cdot \tilde{v}$. This means that the number of lattice sites in FH case has the same value as the number of occupied SLB lattice sites. The FH site is, however, bigger than the SL site to compensate for the volume of the vacancies. Under these conditions the numerator of the right-hand side of Eq. (30) is the FH interaction parameter.

III. RESULTS AND DISCUSSION

A. Calculation of spinodals in the systems PVME/d-PS

In order to determine interaction parameters, spinodals calculated for atmospheric pressure were fitted to the spinodal temperatures^{10,15,16} measured for blends of deuterated polystyrene and poly(vinyl methyl ether) of different molar masses. The scaling parameters and molar masses are listed in Table I. Figure 1 shows the data for normal pressure and mixtures of PVME 89, i.e. the molar mass equals 89 kg/mol, with PS 78.5 or PS 232, respectively. Independent of molar mass of the polystyrenes the adjusted value for ε_{12}^* results to 657.0 K whereas $\delta\varepsilon^*$ is slightly different for the two blends.

The result of the calculations for blends with PVME 64.3 is shown in Fig. 2. Also for this polymer the spinodal temperatures can be calculated with the same value for ε_{12}^* . The calculated critical points shift to higher content of PS with decreasing molar mass of PS as normal.

B. Pressure dependence of spinodals and $\delta\varepsilon^*$

In the following the effect of pressure on the interaction of PVME and PS will be discussed. Figure 3 shows the pressure dependence of the spinodal temperature measured for one composition of one of the blends of Fig. 2, PVME 64.3/d-PS 983 together with two theoretical curves discussed later. The spinodal temperature increases with pressure and the heterogeneous area becomes smaller. $\delta\varepsilon^*$ was adjusted for each pressure and ε_{12}^* was kept constant; whether this procedure is really justified can only be checked by means of additional experimental or theoretical work. Figure 4 shows

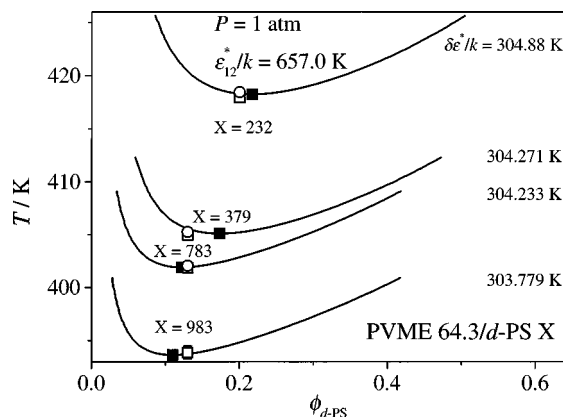


FIG. 2. Spinodals for PVME/d-PS and different molar masses of PS. Open symbols: Data from SANS experiments (Refs. 10 and 16) evaluated assuming mean-field (squares) or 3D-Ising (circles) behavior; solid lines: calculated with the ε_{12}^* and $\delta\varepsilon^*$ values given in the graph; solid squares: calculated critical points.

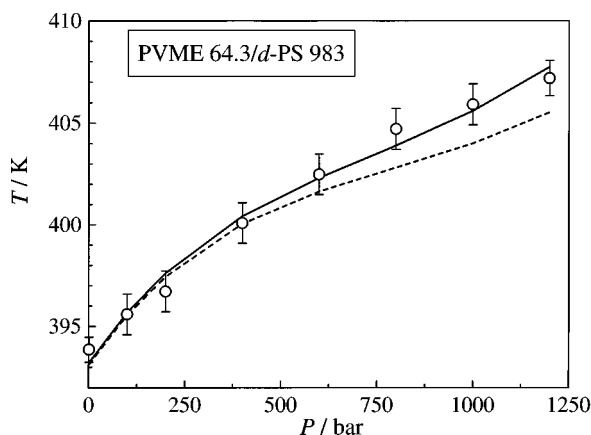


FIG. 3. Pressure dependence of the spinodal temperature for $\phi_{d-PS}=0.13$ [symbols: experimental values (Ref. 10), solid line: calculated] and of the calculated critical temperature (broken line).

the results of this fit. The parameter $\delta\epsilon^*$, quantifying specific interactions, decreases with pressure according to the following relation

$$\delta\epsilon^*/k = 238.552 \text{ K} + 65.208 \text{ K} \exp\left(-\frac{P}{6112.0 \text{ bar}}\right). \quad (31)$$

The solid line in Fig. 3 is calculated with this function for $\delta\epsilon^*$. Since $(\epsilon_{12}^* + \delta\epsilon^*)$ represents the free energy associated with a strong interaction and ϵ_{12}^* is assumed to be independent of pressure, we tentatively apply the following phenomenological thermodynamic relation to the pressure dependence of $\delta\epsilon^*$

$$-\left(\frac{\partial \delta\epsilon^*}{\partial p}\right)_T = \delta V. \quad (32)$$

Although such a treatment is beyond the scope of the SL theory (which does not allow for a change in the volume of lattice sites by pressure), it is obvious from the definition of $\delta\epsilon^*$ as a free energy of contact formation that this quantity

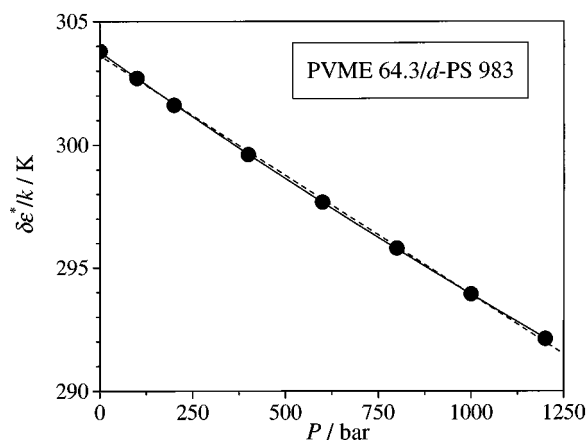


FIG. 4. Pressure dependence of $\delta\epsilon^*$ for PVME 64.3/d-PS 983 ($\epsilon_{12}^*=657$ K) and $\phi_{d-PS}=0.13$. Symbols: values determined from experimental results; solid line: $\delta\epsilon^*$ adjusted according to the fitting function as formulated in Eq. (31); broken line: linear regression.

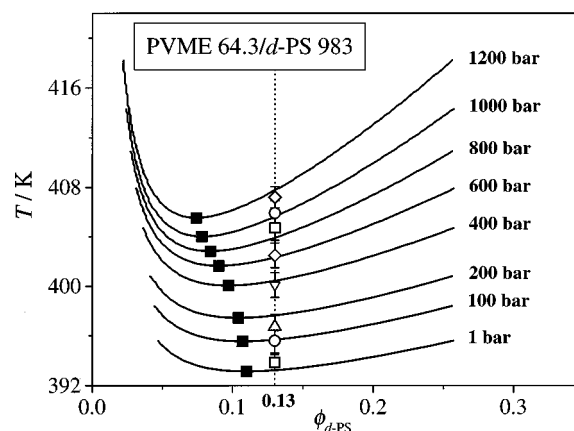


FIG. 5. Spinodals for the system PVME 64.3/d-PS 983 at different pressures. Open symbols: experimental points (Ref. 10); solid squares: calculated critical points with $\epsilon_{12}^*=657$ K and $\delta\epsilon^*$ given by Eq. (31); solid lines: calculated spinodals.

should vary with pressure. The evaluation of the present data according to Eq. (32) yields in good approximation a straight line which corresponds to $\delta V=0.81 \text{ cm}^3/\text{mol}$ (approx. 5% of the cell volume). This result might be taken as an indication that specific interactions require more space than non-specific ones. Further investigation is, however, necessary to check whether the current approach is really meaningful. The spinodals calculated for different pressures with $\delta\epsilon^*/k$ given by Eq. (31) are shown in Fig. 5 together with the experimental data obtained by Janssen *et al.*¹⁰ Since the experimental information is only available for $\phi_{d-PS}=0.13$, there is only one experimental point for each pressure. The calculated critical points shift to higher contents of PVME as the pressure is raised. The pressure dependence of the critical temperature was already shown in Fig. 3 as broken line. It is less pronounced than the shift in the spinodal temperature at a constant blend composition of $\phi_{d-PS}=0.13$. In this context it appears interesting to note that the different curves of Fig. 5 cannot be superimposed by plotting the spinodal temperatures reduced to the critical temperature as a function of the corresponding reduced close packed volume fraction; the curves become slimmer as the pressure increases.

TABLE II. Best-fitted parameters of Eqs. (3) and (4) to the Flory-Huggins interaction parameter calculated by SLB theory in the system PVME 64.3/d-PS 983.

P/bar	A	B	$10^3 \cdot C$	$10^3 \cdot D$
1	0.02069	-0.29024	0.06210	-0.74580
100	0.01931	-0.28538	0.05977	-0.72889
200	0.01799	-0.28110	0.05782	-0.71426
400	0.01545	-0.27396	0.05475	-0.69027
600	0.01298	-0.26832	0.05238	-0.67117
800	0.01057	-0.26392	0.05047	-0.65547
1000	0.00821	-0.26061	0.04891	-0.64229
1200	0.00590	-0.25834	0.04761	-0.63108

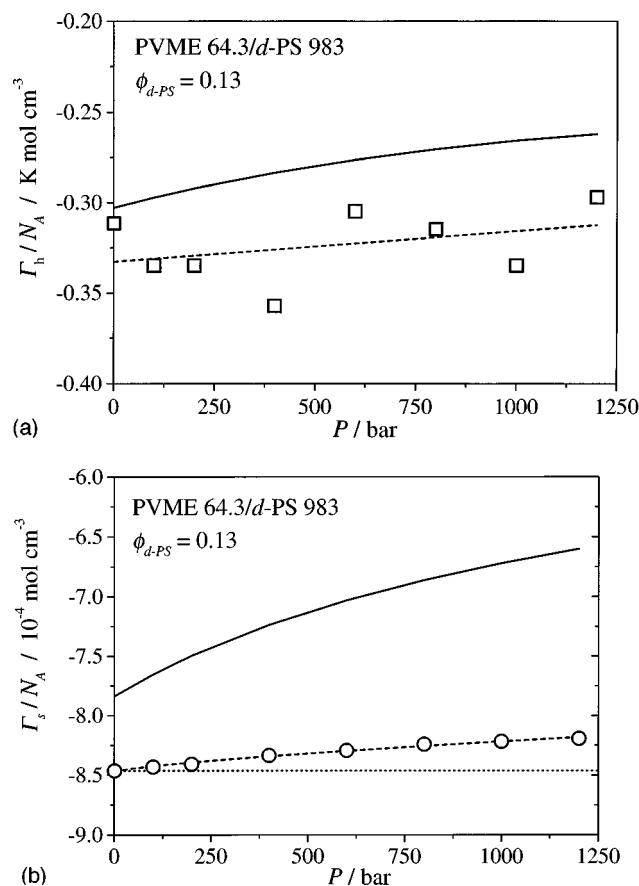


FIG. 6. Enthalpic and entropic contributions to the Flory-Huggins scattering interaction parameter as a function of pressure as obtained from SANS (Ref. 10) (open symbols) and calculated (solid lines) with $\varepsilon_{12}^* = 657 \text{ K}$ and $\delta\varepsilon^*$ given by Eq. (31). (a) Enthalpic contribution Γ_h . (b) Entropic contribution Γ_s .

C. Pressure dependence of the enthalpic and entropic contributions to the scattering interaction parameter

Knowing the SLB parameters the Flory-Huggins interaction parameter, γ can be calculated by means of Eq. (30). This was done in the temperature interval from 350 K to 390 K, identical with the experimental T-range,¹⁰ evaluating the results according to Eqs. (3) and (4) and expressing them in terms of Γ [Eq. (5)]; the corresponding parameters are listed in Table II.

Figure 6 shows the pressure dependencies of the enthalpic and entropic contributions of the scattering interaction parameter calculated by the SLB theory (solid lines) and measured with SANS (Ref. 10) (open symbols).

The agreement between the measured values obtained from the SANS-results and those resulting from the SLB

theory is acceptable for Γ_h , but there is a discrepancy for Γ_s . Janssen *et al.*¹⁰ assume that the reasons are effects not considered by lattice fluid theories.

From Fig. 6(a) it can be seen that Γ_h , the enthalpic contribution to the interaction parameter is nearly independent of pressure as measured and as calculated. On the other hand both, the measured entropic part Γ_s , and that calculated increase noticeably with P [Fig. 6(b)]. Patterson and Robard¹⁷ computed the Flory-Huggins parameter g applying the Prigogine-Flory theory which yields two contributions to g , one scaling with $1/T$ and related to the interactional energy, and a second caused by free volume effects. So the first part corresponds to g_h and the second to g_s . For a polymer-polymer mixture with specific interactions—like that between an aromatic group and an ether group—their calculations for temperatures near the LCST yield an interactional contribution which is nearly independent of the free volume; this means that Γ_h should be nearly independent of pressure. The free volume contribution on the other hand rises considerably as the reduced volume increases. For the influences of pressure this means that the absolute value of Γ_s should decrease markedly. In fact, Figs. 6(a) and 6(b) show that the system PVME/d-PS behaves according to the above considerations. The pressure dependence of Γ_s calculated by SLB is, however, markedly bigger than that obtained from SANS. This overestimation of the free volume effects by SLB may be caused by the fact that all pressure effects were exclusively ascribed to a variation of $\delta\varepsilon$ keeping ε^* constant.

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