A Modified Hole Theory of Polymeric Fluids. 1. Equation of State of Pure Components

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ABSTRACT: The Simha–Somcynsky hole theory of polymeric fluids is here modified in several ways: (1) the Huggins expression replaces that of Flory for the conformational entropy; (2) contact fractions replace site fractions in expressions for the internal energy and for the segmental free length. These modifications produce relatively minor effects on the equation of state of a pure polymer but (as described in the following paper) lead to improved correlations of miscibility behavior.

Introduction

The influence of equation-of-state properties on the thermodynamic behavior of polymer systems has received much attention during the past 25 years. The cell theory of Prigogine[1] had a great impetus, theoretically and experimentally, on thermodynamic research related to polymer systems. Since then, many equation-of-state theories, such as that of Flory, Orwoll, and Vrij,[2-5] have been proposed. These theories identify the relevant parameters responsible for LCST demixing phenomena and the influence of pressure on miscibility. For the present discussion the classical theories can be subdivided into three classes. In a first category we have the cell theories of Flory, Orwoll, and Vrij[2-5] and of Dee and Walsh.[6,7] In these treatments the compressibility and thermal expansion of the system are explained solely by changes in cell volume. In a second group we find the lattice gas model of Koningsveld and Kleintjens[8,9] and the "lattice fluid" theory of Sanchez and Lacombe,[10-12] in which thermal expansion is produced by allowing empty sites on the lattice while the cell volume is assumed to be constant. Finally, we have hole theories, where allowance is made for both cell expansion and lattice vacancies. An example of this type is the Simha–Somcynsky (SS) theory.[13,14] Here the major part of the thermal expansion is due to holes on the lattice; but changes in cell dimension, which have a nonnegligible influence on the thermodynamic properties, are allowed also.

The SS hole theory has been particularly successful in describing properties related to equation-of-state behavior of single and multiconstituent fluids. More recently, the theory has also been applied to the miscibility behavior of polymer solutions and mixtures.[15-18]

In the present work a slightly different hole theory is presented. We believe that the introduction of yet another equation-of-state theory can be justified by the improved and more consistent description and prediction of thermodynamic properties. Especially, the influence of pressure on the phase diagram[19-21] can be extremely complex and, so far, for certain systems has escaped a consistent theoretical explanation. With the molecular model proposed in this paper a consistent theoretical explanation of such complicated thermodynamic data is obtained.

Theory

In hole theories a real system of N molecules in a volume V is modeled on a lattice. Consequently, the chain molecules are defined to consist of s identical segments occupying consecutive sites. However, only a fraction y of the total number of lattice sites is occupied by segments, thus allowing the remaining sites to be vacant. The site fraction is defined by

$$y = Ns/(Ns + N_h) \qquad (1)$$

where N_h is the number of vacant lattice sites.

In the SS theory the site fraction y is the most important structure parameter. However, one can also define a different but related composition variable,[22-25] the (external) contact fraction q. The contact fraction q is a measure for the number of intersegmental contacts the s-mers can make

$$q = N[s(z - 2) + 2]/(N[s(z - 2) + 2] + zN_h) \qquad (2)$$

where z is the lattice coordination number.

The contact fraction is related to the site fraction y by

$$q = (1 - \alpha)y/(1 - \alpha y) \qquad (3)$$

where $\alpha = \gamma(1 - 1/s)$ and $\gamma = 2/z$.

For hole theories the partition function Z is factored in three contributions[26,27]

$$Z = Z_c l_f^{3sNc_s} \exp(-E_0/kT) \qquad (4)$$

where Z_c is the combinatorial entropy arising from the mixing of holes and segments on the lattice, E_0 is the internal energy, and l_f is the segmental free length of an s-mer with $3c_s$ external degrees of freedom per segment.

A. Combinatorial Entropy. The formidable problem of enumerating all the possible configurations available to the s-mers on the lattice was discussed by Meyer,[28] Fowler and Rushbrooke,[29] Chang,[30] Miller,[31] Orr,[32] Huggins,[23-25] Flory,[33-35] Guggenheim,[22] Kurata, Tamura, and Watari,[36] and, more recently, Freed and co-workers.[37] According to the scheme of Flory or Huggins, the total number of configurations is obtained by placing the segments sequentially on the lattice. The possibility of placing a segment at a given lattice site is determined by the probability that the particular lattice site is vacant. In the modified hole theory defined in the present work, the Huggins expression for the combinatorial entropy is used:

$$Z_c = Ns[(1 - y) \ln (1 - y)/y + \ln (y)/s -$$
$$(1 - \alpha y) \ln (1 - \alpha y)/(\gamma y)] \qquad (5)$$

Simha and Somcynsky employed the approximation of Flory, which corresponds to setting $\alpha = 0$. It has been

shown on several occasions that the Huggins entropy, eq 5, constitutes a significant improvement over the Flory expression. It is in much better agreement with Monte Carlo simulations on lattices[37-40] and also improves the description of experimental data.[41] In the Huggins expression the lattice coordination number enters the equations explicitly. However, the coordination number z is here assigned a universal value, and no extra adjustable parameters are introduced.

Further systematic refinements for the combinatorial entropy are available, as shown by Kurata et al.[36] and Freed and Bawendi.[37] However, in these further refinements detailed geometric characteristics of the lattice chosen come into play. In order not to rely too specifically on the lattice concept, these refinements will not be considered here. In fact, the Flory and Huggins expressions can be derived without refering explicitly to a lattice.[42] The only argument one has to apply to obtain these equations is that each segment is surrounded by a number of neighbors; i.e., the fluid is locally ordered. Long-range order, specific to lattices, is not used in the derivations of the equations.

B. Internal Energy. The internal energy E_0 is equated to the lattice energy, which can be expressed as

$$E_0 = N_c \epsilon_c \qquad (6)$$

where ϵ_c is the energy of a contact between two segments and N_c is the number of contacts.

The segmental contact energy ϵ_c is assumed to obey a Lennard-Jones 6–12 potential

$$\epsilon_c = \epsilon^*(A(\omega/v^*)^{-4} - 2B(\omega/v^*)^{-2}) \qquad (7)$$

where $\omega \, (=yV)$ is the cell volume and ϵ^* and v^* are the maximum attraction energy and corresponding segmental repulsive volume, respectively. Due to the long-range character of the interaction potential, the contribution of interactions between non-nearest-neighbor segments is not negligible. In particular, the attractive energy constant B in eq 7 is significantly greater than unity. Unfortunately, the exact contribution of these non-nearest-neighbor interactions depends on the specific lattice used. Following Simha and Somcynsky, we adopt the values $A = 1.011$ and $B = 1.2045$, valid for a face-centered cubic lattice.[43]

The number of contact pairs N_c is given by

$$N_c = N[s(z - 2) + 2]q/2 \qquad (8)$$

The application of the contact fractions q or y results in an additional composition dependency in the lattice energy. Consequently, derived thermodynamic properties, e.g., the χ parameter, become composition dependent also. For rigid lattice models it has been shown that this extra composition dependency of the χ parameter in many cases greatly improves agreement with experiment.[44,45]

Equation 6 for the internal energy reduces to the SS expression if the number of contact pairs is assumed to be determined by the site fraction y

$$N_c = N[s(z - 2) + 2]y/2 \qquad (9)$$

C. Cell Partition Function. The contribution of the cell free volume to the partition function Z is taken as an appropriate average[13] of two extreme free-volume conditions depicted in Figure 1. If all the lattice sites surrounding a central segment are occupied, we can attribute to the central segment a solid-type free volume, determined by the distance of closest approach between two segments (Figure 1a). Since an isolated segment has three degrees of freedom, we can define a solidlike free
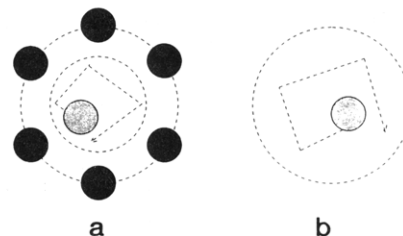

Figure 1. Schematic presentation of the two extreme free-volume conditions: (a) solidlike free length l_s; (b) gaslike free length l_g.

length l_s

$$l_s = (\tilde{\omega}^{1/3} - 2^{-1/6})v^{*1/3} \qquad (10)$$

The other extreme free-volume condition is sketched in Figure 1b. All the lattice sites surrounding the central segment are vacant. In this case the central segment has access to the total cell volume. In this case a gas-type free length l_g can be defined:

$$l_g = \tilde{\omega}^{1/3}v^{*1/3} \qquad (11)$$

In a real system each segment is surrounded by both other segments and vacancies. The free length in this case can be assumed to be an appropriate average of the two extreme conditions. Simha and Somcynsky[13] proposed the site fraction y to be the appropriate averaging parameter:

$$l_f = yl_s + (1 - y)l_g \qquad (12)$$

In the present model, the relevant composition variable is again the contact fraction q, and the segmental free length is defined by

$$l_f = ql_s + (1 - q)l_g \qquad (13)$$

The differences between the present hole theory and the SS theory thus boil down to the systematic substitution of the contact fraction for the site fraction in the derivation of the model.

An important but not exclusive consequence of this maneuver is the substitution of the Huggins combinatorial entropy. In the following, we will refer to the present treatment as the Holes and Huggins (or "Holey Huggins") (HH) theory.

Thermodynamic Properties

A. Helmholtz Free Energy and Equation of State. From the partition function any desired equilibrium thermodynamic property can be obtained. The Helmholtz free energy is given by

$$A = -kT \ln (Z) \qquad (14)$$

In terms of the hole theories the pressure equation becomes

$$p = -(\partial A/\partial V)_{N,T} = -(\partial A/\partial V)_{N,T,y} - (\partial A/\partial y)_{N,T,V}(\partial y/\partial V)_{N,T} \qquad (15)$$

To obtain the equation of state it is necessary to have an expression $(\partial A/\partial y)_{N,T,V}$. At equilibrium, the free energy will be at a minimum value with respect to the structure parameter y:

$$(\partial A/\partial y)_{N,T,V} = 0 \qquad (16)$$

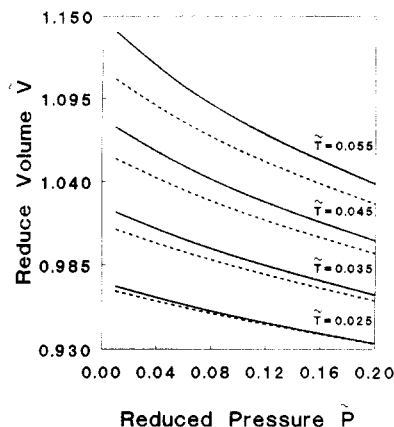For the refined hole (HH) theory, in reduced form, these

Figure 2. Reduced volume $\tilde{V}$ versus reduced pressure $\tilde{P}$ at indicated reduced temperatures $\tilde{T}$ according to Simha–Somcynsky (- - -) and modified hole theory (—).

relations lead to

$$A/(NsRT) = (1 - y) \ln (1 - y)/y + \ln (y)/s - (1 - \alpha y) \times$$
$$\ln (1 - \alpha y)/(\gamma y) - c_s \ln (v^*Q(1 - \eta)^3) + (1 - \alpha)yc_s(AQ^{-4} -$$
$$2BQ^{-2})/(2(1 - \alpha y)\tilde{T}) \quad (17)$$

$$\tilde{P}\tilde{V}/\tilde{T} = 1/(1 - \eta) + 2(1 - \alpha)y(AQ^{-4} - BQ^{-2})/((1 - \alpha y)\tilde{T}) \quad (18)$$

$$0 = (3\eta - 1 + \alpha y)/((1 - \eta)(1 - \alpha y)) + (1 - \alpha)y[2BQ^{-2} -$$
$$3AQ^{-4} + 4\alpha y(AQ^{-4} - BQ^{-2})]/(2\tilde{T}(1 - \alpha y)^2) - c_s(\ln (1 -$$
$$y)/y + 1 - 1/s - \ln (1 - \alpha y)/(\gamma y) - \alpha/\gamma) \quad (19)$$

where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, $\tilde{V} = V/V^*$, $\eta = 2^{-1/6}y(1 - \alpha)/((1 - \alpha y)Q^{1/3})$, and $Q = y\tilde{V}$. The reducing parameters are defined by

$$P^* = z(1 - \alpha)\epsilon^*/v^* \quad (20a)$$

$$V^* = sv^* \quad (20b)$$

$$T^* = z(1 - \alpha)\epsilon^*/c_sR \quad (20c)$$

As expected, eqs 17–19 reduce to the expressions obtained in the SS theory if appropriate changes are made. Furthermore, the SS and HH theories are identical for monomers ($s = 1$). Differences become evident only for molecules of more than one segment. Although the equation of state is dependent only on reduced quantities $\tilde{V}$, $\tilde{T}$, $\tilde{P}$, and y, the minimization condition is explicitly dependent on the chain length s, the flexibility parameter c_s, and the lattice coordination number z. Therefore this theory and the SS theory do not rigorously obey a principle of corresponding states.[13,46] However, for polymers with sufficiently high chain length, a practical principle of corresponding states is obtained.[13]

In Figure 2 reduced isotherms are shown for the SS and HH theories. At higher reduced temperatures differences between them emerge. Clearly, the two theories have different universal PVT surfaces. In Figure 3 it can be observed that the structure parameter y in the same PVT interval is systematically larger for the SS theory; i.e., a denser structure is predicted. In both theories the reduced cell volume shown in Figure 4 is, at a given reduced pressure and temperature, almost identical. Although only slightly dependent on temperature, the cell volume changes more pronouncedly with pressure. At low reduced temperatures $\tilde{T}$ the occupied fraction y approaches unity and the contact fraction q tends to the occupied fraction y. Therefore both treatments can be practically superimposed at low $\tilde{T}$. Because differences are observed on the universal PVT surfaces, it is of interest to see if
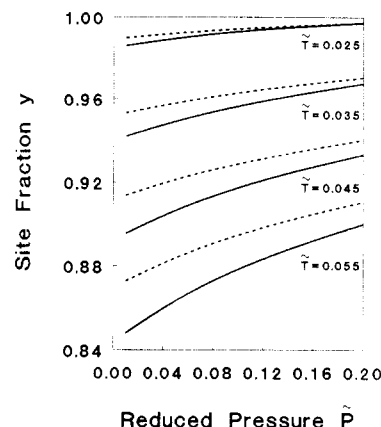

Figure 3. Occupied site fraction y versus reduced pressure $\tilde{P}$ at indicated reduced temperatures $\tilde{T}$ according to Simha–Somcynsky (- - -) and modified hole theory (—).
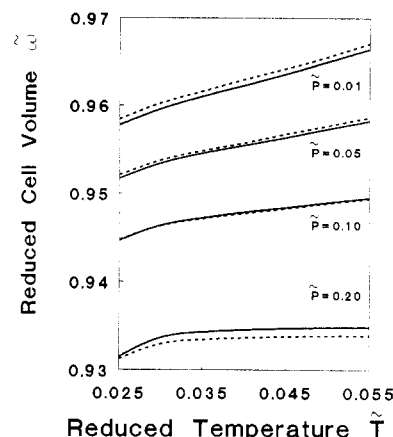

Figure 4. Reduced cell volume $\tilde{\omega}$ versus reduced temperature $\tilde{T}$ at indicated reduced pressures $\tilde{P}$ according to Simha–Somcynsky (- - -) and modified hole theory (—).
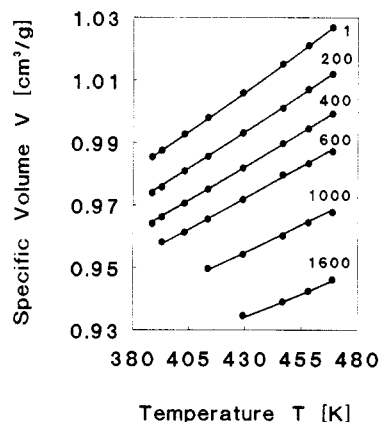

Figure 5. Volume–temperature behavior at indicated pressures (bar) for polystyrene: experimental data[48] (●) and theoretical description according to Simha—Somcynsky (- - -) and modified hole theory (—). Differences between the theoretical descriptions are not visible in this figure.

differences are also noticeable in the description of experimental data.

B. Comparison with Experimental Data. If one is interested in a comparison between theory and experimental data, the relative chain length s has to be defined. Simha and Somcynsky assumed the real molecules to be equivalent to flexible chains for which the following relation exists:[47]

$$c_s = 1/3 + 1/s \quad (21)$$

This assumption then reduces structural differences to

Table I
Molecular and Scaling Parameters According to the Simha–Somcynsky Theory and the Modified Hole Theory[a]

polymer	ϵ^*, J/mol	v^*, 10^{-6} m^3/mol	c_s	P^*, bar	V^*, cm^3/g	T^*, K
		A. Simha–Somcynsky Theory				
polystyrene	6968.8	99.54	0.7694	7002.6	0.9572	10899.2
polyethylene	3356.2	29.68	0.5508	11309.6	1.0581	7330.9
poly(p-chlorostyrene)	9981.0	108.63	1.3361	9189.1	0.7838	8985.8
poly(o-methylstyrene)	8508.1	114.78	0.9591	7416.0	0.9712	10674.2
		B. Modified Hole Theory				
polystyrene	6690.9	98.46	0.8531	6796.6	0.9468	9438.1
polyethylene	3162.9	29.62	0.5834	10679.8	1.0560	6522.4
poly(p-chlorostyrene)	9535.5	107.87	1.4356	8840.8	0.7783	7989.7
poly(o-methylstyrene)	8181.9	113.52	1.0611	7210.8	0.96057	9278.4

[a] Parameters were obtained with eq 22. Thus the segment is taken equal to the monomer unit.

differences in size ratios between effective segment and chemical repeat unit. In the present work a different condition is adopted: the relative chain length is taken equal to the degree of polymerization.

$$s = M/M_0 \qquad (22)$$

where M is the molar mass of the polymer and M_0 is the molar mass of the repeating unit.

In Figure 5 experimental PVT data for PS are shown.[48] Differences between the SS and HH theories are numerically small and would not be visible in this figure. Also, differences in computed thermal expansion and compressibility coefficients are very small. Nevertheless the polymer is modeled differently in both theories. For PS and some other polymers the molecular parameters and scaling parameters obtained from experimental equation-of-state data[48-50] and condition 22 are summarized in Table I. The parameters are extracted from the experimental data with a multiparameter estimation program[51] developed at DSM, The Netherlands. In all computations the segment was taken equal to the monomer unit. Consequently, the parameter values shown in Table Ia are different from literature values, which in all cases were obtained[52] with eq 21.

For the systems considered in Table I the values of the scaling parameters P^*, V^*, and T^* are larger for the SS theory than for the HH theory. Consequently, the polymer is situated in different regions of the universal PVT surface. The differences in the scaling parameter values are of course related to differences in the molecular parameters obtained from the experimental PVT data. In the SS treatment the interaction parameters ϵ^* and v^* are larger, indicating a deeper and wider potential bowl than for the HH model.

On the other hand, the Prigogine parameter c_s is smaller, indicating that fewer degrees of freedom are volume dependent in the SS theory. From the changes in the molecular parameters one can anticipate a denser structure for the SS theory compared to the HH theory. This is confirmed by the computations. It is worthwhile to observe that the flexibility parameter c_s can become larger than unity, indicating that the monomeric segments are not rigid spheres but have some degrees of freedom dependent on volume. With condition 21 values for the flexibility parameter are always smaller than unity. In this case the segment size is considerably smaller than the monomer size. The changes in the Prigogine parameter c_s, resulting from the use of eq 21 or 22 are closely correlated to the observed changes in segmental volume.

Conclusions

The HH and SS theories produce similar predictions of the equation-of-state behavior of polymer systems.

However, differences are noticeable if one considers how a real system is modeled. The HH theory suggests a less dense structure, i.e., a larger fraction of holes on the lattice. This is realized by adopting a slightly shallower bowl in the interaction potential. However, the most important factor responsible for the introduction of extra holes in the structure is the increased number of external degrees of freedom. Furthermore, the separate contributions of the entropy and energy to the free energy are significantly different for both models. Although no significant differences are observed in the description of equation-of-state data, more important differences are found if one is concerned with the description and prediction of compositional derivatives, i.e., properties related to miscibility. This is elaborated in the following paper.

References and Notes

(1) Prigogine, I.; Bellemans, A.; Mathot, V. *The Molecular Theory of Solutions*; North-Holland Publishing Co.: Amsterdam, 1957.
(2) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3567.
(3) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(4) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *65*, 2035.
(5) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.
(6) Dee, G. T.; Walsh, D. J. *Macromolecules* **1988**, *21*, 811.
(7) Dee, G. T.; Walsh, D. J. *Macromolecules* **1988**, *21*, 815.
(8) Kleintjens, L. A.; Koningsveld, R. *J. Electrochem. Soc.* **1980**, *121*, 2353.
(9) Kleintjens, L. A.; Koningsveld, R. *Colloid Polym. Sci.* **1980**, *258*, 711.
(10) Sanchez, I. C.; Lacombe, R. U. *J. Phys. Chem.* **1976**, *80*, 2352.
(11) Sanchez, I. C.; Lacombe, R. U. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *15*, 17.
(12) Lacombe, R. U.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(13) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 341.
(14) Jain, R. K.; Simha, R. *Macromolecules* **1980**, *13*, 1501.
(15) Jain, R. K.; Simha, R. *Macromolecules* **1984**, *17*, 2663.
(16) Simha, R.; Jain, R. K. *Polym. Eng. Sci.* **1984**, *24*, 1284.
(17) Stroeks, A.; Nies, E. *Polym. Eng. Sci.* **1988**, *23*, 1284.
(18) Nies, E.; Stroeks, A.; Simha, R.; Jain, R. K., accepted for publication in *Colloid Polym. Sci.*
(19) Wolf, B. A.; Geerissen, H. *Colloid Polym. Sci.* **1981**, *259*, 1214.
(20) Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Polymer* **1975**, *16*, 445.
(21) Suzuki, Y.; Miyamoto, Y.; Miyaji, H.; Asai, K. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 563.
(22) Guggenheim, E. A. *Proc. R. Soc. London A* **1944**, *183*, 203.
(23) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
(24) Huggins, M. L. *J. Phys. Chem.* **1942**, *46*, 151.
(25) Huggins, M. L. *Ann. N.Y. Acad. Sci.* **1943**, *44*, 431.
(26) See ref 1, p 140.
(27) Hirschfelder, J. O.; Curtiss, E. F.; Bird, R. B. *The Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
(28) Meyer, K. H. *Z. Phys. Chem., Abt. B* **1934**, *34*, 383.

(29) Fowler, R. H.; Rushbrooke, G. S. *Trans. Faraday Soc.* **1933**, *33*, 1272.
(30) Chang, T. S. *Proc. Cambridge R. Soc.* **1939**, *35*, 265.
(31) Miller, A. R. *Proc. Cambridge R. Soc.* **1942**, *38*, 109.
(32) Orr, W. J. C. *Trans. Faraday Soc.* **1944**, *40*, 307.
(33) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660.
(34) Flory, P. J. *Proc. R. Soc. London, A* **1956**, *234*, 60.
(35) Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1942**, *79*, 4510.
(36) Kurata, M.; Tamura, M.; Watari, T. *J. Chem. Phys.* **1955**, *23*, 991.
(37) Freed, K. F.; Bawendi, M. G. *J. Phys. Chem.* **1989**, *93*, 2194.
(38) Okamoto, H. *J. Chem. Phys.* **1979**, *70*, 1690.
(39) Bellemans, A.; De Vos, E. *J. Polym. Sci., Part C, Polym. Symp.* **1973**, *42*, 1195.
(40) Dickman, R.; Hall, C. K. *J. Chem. Phys.* **1986**, *85*, 3023.
(41) Irvine, P.; Gordon, M. *Macromolecules* **1980**, *13*, 761.
(42) Longuet-Higgins, H. C. *Proc. R. Soc. London* **1951**, *A205*, 247.

(43) Jones, J. E.; Ingham, A. E. *Proc. R. Soc. London* **1925**, *A107*, 636.
(44) Koningsveld, R.; Kleintjens, L. A. *Macromolecules* **1971**, *4*, 637.
(45) Nies, E.; Koningsveld, R.; Kleintjens, L. A. *Prog. Colloid Polym. Sci.* **1985**, *17*, 2.
(46) Nanda, V. S.; Simha, R.; Somcynsky, T. *J. Polym. Sci., Part C, Polym. Symp.* **1966**, *12*, 277.
(47) See ref 1, pp 323–334.
(48) Quach, A.; Simha, R. *J. Appl. Phys.* **1971**, *42*, 4592.
(49) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 205.
(50) Walsh, D. J. Central Research and Development Department, E. I. du Pont de Nemours & Co. Inc., Wilmington, DE 19898, private communication.
(51) Hillegers, L. T. M. E. The estimation of parameters in functional relationship models. Dissertation, 1986, Eindhoven University of Technology, The Netherlands.
(52) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 211.

A Modified Hole Theory of Polymeric Fluids. 2. Miscibility Behavior and Pressure Dependence of the System Polystyrene/Cyclohexane

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ABSTRACT: Experimental miscibility behavior and the influence of pressure upon it are discussed with the modified hole theory introduced in the previous paper. For the first time the complicated pressure dependence for the system polystyrene/cyclohexane is theoretically reproduced. The modified hole theory and Simha-Somcynsky hole theory are compared. Thermodynamically the pressure dependence of the critical temperature is related to the compositional curvature of the volume of mixing. According to the modified hole theory a complicated composition dependence for the volume of mixing is predicted as a result of a delicate interplay of two volume effects. Spanning the complete composition range a volume contraction is predicted directly related to the change in the structure parameter defined in the hole theory. However, this overall contraction is perturbed by a volume expansion related to the packing efficiency of different component segments. These two distinct volume contributions result in a complicated dependence of the volume of mixing on composition and set the hole theories apart from other equation-of-state theories currently available.

Introduction

Since the pioneering work of Flory,[1-3] Huggins,[4-6] and Prigogine,[7] a vast number of publications has been devoted to the study of upper (UCMT) and lower critical miscibility temperature (LCMT) phase behavior in relation to different thermodynamic and molecular parameters. Basically, for nonpolar polymer systems (thus excluding systems with strong orientation-dependent interactions) the UCMT demixing is a result of entropic contributions to the free energy favoring miscibility at high temperatures and unfavorable energetic interactions ultimately causing the system to demix at sufficiently low temperatures.[8] The entropically driven LCMT demixing is essentially due to a mismatch between the equation-of-state properties of the constituents.[8] The discussion of strong orientational interactions can be successful only when different theoretical concepts are applied.[7,9] Therefore, in the present paper only nonpolar systems will be discussed. The basic ingredients, i.e., combinatorial entropy and energetic and equation-of-state contributions, not only provide a sound theoretical framework to discuss phase behavior at atmospheric pressure but also allow the evaluation of, e.g., excess functions and the influence of pressure on thermodynamic properties. Independent of any particular model, thermodynamic correlations of course exist between the excess enthalpy and volume and the pressure dependence on the phase behavior.[8] These correlations bring to bear a thorough test upon the molecular theories at hand. Partly to test these relations the influence of pressure on the phase behavior for different polymer solutions and blends has been documented experimentally.[10-12] Some current theories are not capable of correlating these data.[10,11] In this work the Simha-Somcynsky hole theory[13] and a modified hole theory[14] are used to discuss the experimental data. With the modified hole theory a consistent prediction of all the data available for the system polystyrene/cyclohexane is obtained.

Theory

A. Helmholtz Free Energy. The hole theory for pure components discussed in the previous paper[14] is readily extended to mixtures. For a binary mixture of N_a and N_b molecules of component A and B, respectively, in a volume