Macromolecules **1995,** *28,* 7737−7743

Open-Cell Model Equation of State for Liquids. 2. Polymer Solutions and Blends

Chongli Zhong, Wenchuan Wang,* and Huanzhang Lu

Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Received August 24, 1994; Revised Manuscript Received August 7, 1995[⊗]

ABSTRACT: The open-cell model equation of state (OCM EOS) proposed in the preceding paper by the authors has been extended to polymer−solvent and polymer blend systems, covering a variety properties, including $P-V-T$ relations, the excess volume and enthalpy, the activity of solvents, and phase diagrams. Compared with the well-recognized Simha and Somcynsky EOS, the OCM EOS presents a better description of $P-V-T$ relations and phase diagrams. Besides, through a set of proper binary interaction parameters, good correlation of the excess properties can be achieved. In conclusion, as an improvement over the existing hole theory EOSs, the OCM EOS is capable of describing liquid mixture properties with satisfactory accuracy.

1. Introduction

In our preceding paper,[1] an open-cell concept was introduced. A new free volume expression and the open-cell model equation of state (OCM EOS) were derived. This EOS was successfully used to describe the $P-V-T$ behavior for liquids, including 15 polymers, 17 higher molecular weight hydrocarbons, and 10 organic solvents. To test the OCM EOS more rigorously, we extend it to liquid mixtures, mainly polymer−solvent systems and polymer blends, in this work. $P-V-T$ relations, the excess volumes and enthalpies, activities of solvents in polymers, and phase diagrams for polymer solutions and blends are estimated in terms of the properties of pure substances and the mixing rules proposed. The calculated results are also compared with those from the well-recognized Simha and Somcynsky EOS.[2]

2. OCM EOS for Mixtures

Similar to the derivation of the OCM EOS[1] and Jain and Simha,[3] the configurational partition function for a random mixing system consisting of N_i molecules and i components (i = 1, 2, ...) is given by

$$Z = \left[\frac{2\pi\langle M_0\rangle RT}{(N_a h)^2}\right]^{3/2\sum N_i s_i c_{si}} g V_f^{\sum N_i s_i c_{si}}\, e^{-E_0/kT} \tag{1}$$

where $\langle M_0\rangle$ is the average segmental molecular weight, s_i is the number of segments of molecule i, and N_a, h, and k are the Avogadro, Planck, and Boltzmann constants, respectively. $3c_{si}$ is the number of external degrees of freedom per segment for molecule i.

In eq 1, g represents the combinatorial factor, V_f the free volume, and E_0 the lattice energy. Continuing with the assumption of random mixing throughout, g is given by[3]

$$\ln g = -\sum N_i \ln N_i + \sum (s_i - 1) N_i \ln\left[\frac{(z-1)}{e}\right] + \sum N_i \ln\left[\sum (N_i s_i)\right] - \sum N_i \ln y - \sum (s_i N_i)\left[\frac{(1-y)\ln(1-y)}{y}\right] \tag{2}$$

V_f and E_0 are expressed as

$$\ln V_f^{\sum N_i s_i c_{si}} = \sum N_i s_i c_{si} [\ln(w^{1/3} - 0.8909 y \langle v^*\rangle^{1/3})^3 + RR] \tag{3}$$

$$\frac{E_0}{kT} = \frac{y \sum N_i q_i z s_i}{2kT} \langle \epsilon^* \rangle \left[1.011\left(\frac{\langle v^*\rangle}{w}\right)^4 - 2.405\left(\frac{\langle v^*\rangle}{w}\right)^2\right] \tag{4}$$

where $\langle \epsilon^*\rangle$ and $\langle v^*\rangle$ are the characteristic energy and volume parameters, $q_i z$ is the number of nearest-neighbor sites per chain for molecule i, y is the occupied-site fraction, and w is the cell volume. z is the coordination number, which is set to 12 here. RR is defined later. All the variables with brackets signify the average properties for a mixture. Therefore, for a binary system

$$\langle s\rangle^{-1} = \phi_1/s_1 + \phi_2/s_2 \tag{5}$$

$$\langle C_s\rangle = \phi_1 C_{s1} + \phi_2 C_{s2} \tag{6}$$

$$\langle M_0\rangle = \phi_1 M_{01} + \phi_2 M_{02} \tag{7}$$

$$\langle V^*\rangle = \phi_1^2 V_{11}^* + 2\phi_1\phi_2 V_{12}^* + \phi_2^2 V_{22}^* \tag{8}$$

$$\langle \epsilon^*\rangle = \phi_1^2 \epsilon_{11}^* + 2\theta_1\theta_2 \epsilon_{12}^* + \theta_2^2 \epsilon_{22}^* \tag{9}$$

$$\theta_i = \frac{\phi_i q_i z}{\langle qz\rangle} \tag{10}$$

$$\langle qz\rangle = \phi_1 q_1 z + \phi_2 q_2 z \tag{11}$$

$$q_i z = z - 2 + 2/s_i \tag{12}$$

where subscripts 1 and 2 represent components 1 and 2, respectively.

As a result, the Helmholtz free energy A for a binary mixture consisting of N_1 and N_2 molecules of components 1 and 2, respectively, can be derived from the

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

0024-9297/95/2228-7737$09.00/0

Table 1. Pure Component Parameters for the *P-V-T* Calculation of Mixtures

component	T^* (K)	P^* (MPa)	V^* (cm^3/g)	β	C_s	M_0 (g/mol)	data source
PIB	13161	656.9	1.1110	0.2	0.333	49.3	15
PDMS	9249	481.4	0.9770	0.2	0.333	53.8	15
PS	14426	755.4	0.9796	0.2	0.333	53.3	16
PPO	13541	853.5	0.9015	0.2	0.333	48.1	16
benzene	7871	827.0	1.0418	0.2	0.668	50.1	17
cyclohexane	8182	658.8	1.1966	0.2	0.588	50.1	18
HMDS	7367	454.2	1.1676	0.2	0.475	54.1	19

thermodynamic relation $A = -kT \ln Z$ as

$$\frac{A_\phi}{RT} = \frac{A}{(N_1 s_1 + N_2 s_2)\, kT} = \frac{\phi_1}{s_1} \ln \frac{\phi_1}{s_1} + \frac{\phi_2}{s_2} \ln \frac{\phi_2}{s_2} - \frac{\langle s \rangle - 1}{\langle s \rangle} \ln\left[\frac{(z-1)}{\mathrm{e}}\right] + \frac{\ln y}{\langle s \rangle} + \frac{(1-y)}{y} \ln(1-y) - \langle C_s \rangle \left[\ln\left[\frac{\langle v^* \rangle (1-W)^3}{Q}\right] + \frac{3}{2} \ln\left[\frac{2\pi \langle M_0 \rangle RT}{(N_a h)^2}\right] + RR - \frac{yQ^2(1.011Q^2 - 2.409)}{2\bar{T}} \right] \tag{13}$$

where A_ϕ denotes the Helmholtz free energy per mole of segment, ϕ the segment fraction, and

$$Q = (y\bar{V})^{-1} \tag{14}$$

$$W = 0.8909 y Q^{1/3} \tag{15}$$

The combining rules are introduced here for the cross characteristic energy and volume in eqs 8 and 9:

$$\epsilon_{12}^* = \zeta(\epsilon_{11}^* \epsilon_{22}^*)^{0.5} \tag{16}$$

$$V_{12}^* = \eta[(v_{11}^{*1/3} + v_{22}^{*1/3})/2]^3 \tag{17}$$

where ζ and η are two adjustable binary interaction parameters.

The variable RR in eq 3 is here defined as

$$RR = \ln\left[1 + 10.7\langle\beta\rangle \frac{1-y}{y} \exp\left[-\frac{0.0052\langle c_s \rangle y}{2\bar{T}(1-y)}\right]\right] \tag{18}$$

where the so-called spatial structure parameter $\langle\beta\rangle$[1] for a binary mixture is

$$\langle\beta\rangle = \phi_1^2 \beta_1 + 2\phi_1\phi_2\beta_{12} + \phi_2^2\beta_2 \tag{19}$$

The cross parameter β_{12} is given by

$$\beta_{12} = \xi(\beta_1 + \beta_2)/2 \tag{20}$$

where β_1 and β_2 are the spatial parameters for components 1 and 2, respectively. ξ is another binary interaction parameter. As mentioned by Zhong, Wang, and Lu,[1] for most substances they have calculated, β can be set to a constant, 0.2. In these cases, ξ is equal to unity; eq 20 is therefore simplified to

$$\langle\beta\rangle = \phi_1\beta_1 + \phi_2\beta_2 \tag{21}$$

Similar to the derivations for pure substances, the occupied-site fraction y in the lattice for a mixture can be obtained by minimizing the Helmholtz free energy, i.e., $(\partial A/\partial y)_{T,V} = 0$. After rearrangements, an implicit expression for y is obtained:

$$\left[\frac{(\langle s \rangle - 1)}{\langle s \rangle} + y^{-1}\ln(1-y)\right]/3\langle c_s \rangle = \frac{y}{6\bar{T}(y\bar{V})^2}[2.405 - 3.033(y\bar{V})^{-2}] + \left[2^{-1/6} y (y\bar{V})^{-1/3} - \frac{1}{3}\right][1 - 2^{-1/6} y (y\bar{V})^{-1/3}]^{-1} + \bar{R}\bar{R} \tag{22}$$

where

$$\bar{R}\bar{R} = \frac{1+U}{3y(10.7\langle\beta\rangle)^{-1}\mathrm{e}^U + 3(1-y)}, \qquad U = \frac{0.0052\langle c_s \rangle y}{2\bar{T}(1-y)} \tag{23}$$

From the fundamental thermodynamic equation, $P = -(\partial A/\partial V)_{T,N_1,N_2}$, the OCM EOS for a mixture is derived:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = [1 - 2^{-1/6} y (y\bar{V})^{-1/3}]^{-1} + \frac{2y}{\bar{T}(y\bar{V})^2}[1.011(y\bar{V})^{-2} - 1.2045] \tag{24}$$

where y can be solved in terms of eq 22, and the reduced temperature, volume, and pressure are given by

$$\begin{aligned} \bar{T} &= T/T^*; & T^* &= \langle qz \rangle \langle \epsilon^* \rangle / \langle c_s \rangle R \\ \bar{P} &= P/P^*; & P^* &= \langle qz \rangle \langle \epsilon^* \rangle / \langle v^* \rangle \\ \bar{V} &= V/V^*; & V^* &= \langle v^* \rangle / \langle M_0 \rangle \end{aligned} \tag{25}$$

3. Results

We have extensively tested the OCM EOS for various polymer–solvent and polymer blend mixture systems, covering a variety of properties, including $P-V-T$ relations, the excess volumes and enthalpies, activities of solvents, and phase diagrams. In our calculations, the results from the Simha–Somcynsky EOS (SS EOS) are also shown in parallel with ours, since the SS EOS has been evaluated by Dee and Walsh[4] and Rodgers[5] as one of the best among many liquid EOSs, including the Flory et al.,[6] modified cell model,[7] and Sanchez–Lacombe EOSs.[8]

(1) *P–V–T* Relations for Polymer–Solvent and Polymer Blend Systems. We have carried out calculations for four polymer–solvent and one polymer blend system (see Table 2). All the parameters for pure substances are listed in Table 1, which are obtained by the method recommended in our preceding paper.[1] As is seen in Table 2, the binary interaction parameters are regressed at different compositions. In most cases, the spatial structure parameter β can be treated as a constant, 0.2;[1] the parameter ξ is therefore set to unity with no effect on the results. It is, however, worth noticing that for some binary systems whose β values for the constituent components are not a constant, 0.2, or the components are rather asymmetric molecules, e.g., the PDMS + cyclohexane system in this work, ξ should be considered a regressed parameter rather than unity (see Table 2).

From the calculated density average absolute deviations (AADs; see the definition in Table 2), it is found that the OCM EOS provides better results than the SS EOS. If the parameter ξ is considered as composition dependent, remarkable improvement can be obtained for some systems. For example, the liquid density AAD

Table 2. Results for the *P-V-T* Calculation of Mixtures and the Interaction Parameters Regressed for Constant Compositions

					OCM EOS				SS EOS	
mixture	composition ϕ_1	temp range (°C)	press. range (MPa)	no. of data points	ζ	η	ξ	AAD ρ^a	AAD ρ	data source
PIB–cyclohexane	0.1971	25–65	0.1–100	55	0.8547	0.9004	1.000	0.011	0.025	5
	0.3731	25–65	0.1–100	55	0.9493	0.9620	1.000	0.023	0.039	
	0.5445	25–65	0.1–100	55	0.9616	0.9790	1.000	0.014	0.026	
PIB–benzene	0.1989	25–65	0.1–100	55	0.9531	1.0015	1.000	0.023	0.075	5
	0.4355	25–65	0.1–100	55	0.8235	0.9967	−0.402	0.030	0.101	
	0.5923	25–65	0.1–100	55	0.9666	1.0004	1.000	0.023	0.044	
PDMS–cyclohexane	0.5017	25–65	0.1–100	55	0.8624	0.9476	−0.158	0.016	0.077	5
PDMS–HMDS	0.4370	25–65	0.1–100	55	0.9835	0.9475	1.000	0.030	0.040	5
PPO–PST^b	0.2	140–300	0.1–180	62	0.9900	1.0065	1.000	0.037	0.026	16
	0.4	140–300	0.1–180	49	0.9757	0.9901	1.000	0.032	0.038	
	0.5	180–320	0.1–180	56	0.9258	0.9887	0.407	0.041	0.065	
	0.6	180–300	0.1–180	42	0.8512	0.9468	−0.028	0.036	0.094	
	0.8	220–340	0.1–180	53	0.9463	0.9853	1.000	0.067	0.072	
grand ave								0.029	0.056	

[a] AAD $\rho = (1/N)\Sigma|\rho_i^{\mathrm{calc}} - \rho_i^{\mathrm{exp}}|/\rho_i^{\mathrm{exp}} \times 100$. [b] The compositions are weight fractions of PPO; the others are volume fractions of polymers.

Table 3. Results for the *P-V-T* Calculation of Mixtures and the Interaction Parameters Regressed over the Entire Range of Compositions

		OCM EOS			
mixture	comp range ϕ_1	ζ	η	ξ	ADD ρ^a
PIB-cyclohexane^b	0.1971–0.5445	0.9912	0.9661	1.000	0.70
PIB–benzene^b	0.1989–0.5923	0.9612	1.0008	1.000	0.08
PPO–PS^c	0.2–0.8	0.9723	0.9759	1.000	0.70
grand ave					0.49

[a] AAD $\rho = (1/N)\Sigma|\rho_i^{\mathrm{calc}} - \rho_i^{\mathrm{exp}}|/\rho_i^{\mathrm{exp}} \times 100$. [b] The compositions are volume fractions. [c] The compositions are weight fractions.

Table 4. Comparison between Experimental and Calculated Excess Volume with Parameters in Table 3 for the PIB + benzene System

		V^E (cm^3/cm^3)	
temp (K)	wt frac of polymer w_1	expt	calc
297.65	0.6352	0.00341	0.00246
297.65	0.5299	0.00340	0.00294
297.65	0.4379	0.00343	0.00315

Table 5. Comparison between Experimental and Calculated Excess Enthalpy with Parameters in Table 3 for the PIB + benzene System

		H^E (cal/g)	
temp (K)	vol frac of polymer ϕ_1	expt	calc
298.15	0.0071	4.739	9.870
298.15	0.0139	4.822	9.856
298.15	0.0169	4.768	9.838
298.15	0.0191	4.802	9.823
298.15	0.0230	4.700	9.793
298.15	0.0249	4.675	9.778
298.15	0.0279	4.807	9.753
298.15	0.0286	4.660	9.747
298.15	0.0347	4.595	9.694
298.15	0.0367	4.594	9.677
298.15	0.0377	4.722	9.668
298.15	0.0593	4.592	9.473

for polyisobutylene (PIB) + benzene at $\phi_1 = 0.4355$ decreases to 0.03% for the OCM EOS versus 0.101% for the SS EOS. Similarly, for the poly(dimethylsiloxane) (PDMS) + cyclohexane system and the poly(2,6-dimethyl-1,4-phenylene ether) (PPO) + polystyrene (PS) blend, the OCM EOS presents better accuracy.

To investigate the composition dependence of the binary interaction parameters, we have calculated three systems, PIB + cyclohexane, PIB + benzene, and PPO + PS, in terms of the parameters regressed from the entire concentration range. Besides, ξ is set to unity for these three systems. From Table 3 we have found that though there are some accuracy losses compared with the results in Table 2, the AADs for mixture liquid densities are still acceptable.

(2) Excess Volume and Enthalpy. The excess properties are important thermodynamic functions for nonideal solutions. As pointed out by Renuncio and Prausnitz,[9] it is difficult to correlate both the excess volume and excess enthalpy using one set of parameters in EOSs. To test the capability of the OCM EOS, we have investigated two systems, PIB + benzene and PIB + cyclohexane.

From the definitions of the excess properties, the excess volume, V^E, and excess enthalpy, H^E, for a binary system are given by

$$V^E = V^m - w_1 V_1 - w_2 V_2 \tag{26}$$

and

$$H_\phi{}^E = H_\phi{}^m - \phi_1 H_1 - \phi_2 H_2 \tag{27}$$

where V^E, V^m, and V are the excess, mixture, and pure substance volume per weight, respectively. w represents the weight fraction, $H_\phi{}^E$, $H_\phi{}^m$, and H are excess, mixture, and pure substance enthalpy per mole of segment, respectively. $H_\phi{}^E$ can be calculated by the method in Appendix A.

We have first calculated V^E and H^E for PIB + benzene systems in terms of the binary interaction parameters regressed from $P-V-T$ data (see Table 2). Tables 4 and 5 indicate that the predicted V^E values are in fair agreement with the experimental data. In contrast, the predicted H^E values are not satisfactory. Thus we have attempted to correlate both V^E and H^E using the parameters ζ, η, and ξ regressed their experimental data. Tables 6 and 7 show that, in this case, the OCM EOS can be used for the correlation of both V^E and H^E with good accuracy. The results for PIB + cyclohexane are also listed in Tables 6 and 7. Obviously, AADs for H^E of PIB + cyclohexane are somewhat larger. We have not tested this system further due to a lack of data.

In the view of thermodynamic consistency, if a model is reasonable, there should be a set of parameters to well correlate $P-V-T$, V^E, and H^E as well as other properties simultaneously. To explore the applicability of the parameters in Table 6 to other properties, they have been used to calculate $P-V-T$ for the two systems of interest. As a result, the liquid density AADs are 0.09 and 1.36% for PIB + benzene and PIB + cyclohex-

Table 6. Comparison between Experimental and Calculated Excess Volume with Parameters Regressed from both Excess Volume and Excess Enthalpy Data

system	temp (K)	wt frac of polymer w_1	parameters ζ	η	ξ	V^E (cm^3/cm^3) expt	OCM
PIB + benzene	297.65	0.6352	0.9697	1.0087	0.7183	0.00341	0.00333
	297.65	0.5299				0.00340	0.00350
	297.65	0.4379				0.00343	0.00335
AAD[a]							2.44
PIB + cyclohexane	298.15	0.6522	0.9938	1.0077	0.9630	−0.00136	−0.00134
	298.15	0.5681				−0.00141	−0.00145
	298.15	0.3470				−0.00141	−0.00137
AAD							2.38

[a] AAD = $(1/N)\Sigma|V^E_{\mathrm{calc}} - V^E_{\mathrm{exp}}|/V^E_{\mathrm{exp}} \times 100.$)

Table 7. Comparison between Experimental and Calculated Excess Enthalpy with Parameters Regressed from both Excess Volume and Excess Enthalpy Data

system	temp (K)	vol frac of polymer ϕ_1	H^E (cal/g) expt	OCM
PIB + benzene	298.15	0.0071	4.739	4.679
	298.15	0.0139	4.822	4.714
	298.15	0.0169	4.768	4.717
	298.15	0.0191	4.802	4.717
	298.15	0.0230	4.700	4.715
	298.15	0.0249	4.675	4.713
	298.15	0.0279	4.807	4.709
	298.15	0.0286	4.660	4.708
	298.15	0.0347	4.595	4.698
	298.15	0.0367	4.594	4.695
	298.15	0.0377	4.722	4.693
	298.15	0.0593	4.592	4.649
AAD[a]				1.40
PIB + cyclohexane	298.15	0.0321	−0.139	−0.169
	298.15	0.0324	−0.222	−0.169
AAD				22.75

[a] AAD = $(1/N)\Sigma|H^E_{\mathrm{calc}} - H^E_{\mathrm{exp}}|/H^E_{\mathrm{exp}} \times 100.$

ane, respectively. Compared with the AADs simply from the $P-V-T$ calculations in Table 2, 0.08 and 0.70, respectively, no significant accuracy losses have been found. This observation indicates that there exists a set of parameters in the OCM EOS that can be used to correlate $P-V-T$, V^E, and H^E simultaneously with satisfactory accuracy. However, because of the multiple valued characteristics, a proper set of parameters should be searched carefully. Meanwhile, a compromise among the accuracies for different properties has to be taken into account.

(3) Activities of Solvents for Polymer Solutions. For polymer–solvent systems, the activity of the solvent in a binary system is

$$\mu_2 - \mu_2^\circ = RT \ln a_2 \tag{28}$$

where μ_2° and μ_2 represent the chemical potentials for the pure solvent and the solvent in the binary solution, respectively. a_2 is the activity of the solvent. For a pseudobinary polymer solution

$$\mu_2 = G_\phi S_2 - S_2\phi_1\left(\frac{\partial G_\phi}{\partial \phi_1}\right)_{T,P} \tag{29}$$

where S_2 is the number of segments of the solvent, ϕ_1 is the segmental fraction of the polymer, and G_ϕ is the molar segmental Gibbs free energy, $=A_\phi + PV_\phi$, in which V_ϕ denotes the molar segmental volume. Derivation of $(\partial G_\phi/\partial\phi_1)_{T,V}$ is given in Appendix B.

We have carried out calculations for seven polymer solutions (Table 9). All the parameters for the pure substances of interest can be found in either Table 1 or Table 8. All the binary interaction parameters in Table 9 are regressed by fitting the experimental solvent activity data. For most systems, the AADs for the calculated activities of the solvents (definition is given in Table 9) are less than 0.5%. Though the AADs for PIB + pentane and PIB + benzene are somewhat larger, 1.63 and 1.08%, respectively, the results are, in general, quite satisfactory.

Table 8. Pure Component Parameters for the Activity Calculation of Solvent for Polymer Solutions

component	T^* (K)	P^* (MPa)	V^* (cm^3/g)	C_s	M_0 (g/mol)	data source
PB	10884	750.9	1.0970	0.333	36.1	20
PEO	10152	632.1	0.8614	0.333	51.0	21
PO	13870	852.0	0.8731	0.333	51.0	22
pentane	6936	497.6	1.3926	0.623	50.1	17
octane	8065	578.1	1.3166	0.524	45.6	23

(4) Phase Diagrams. The description of phase diagrams for polymer solutions of theoretical and practical importance. We have used the OCM EOS to calculate the phase diagrams for four polymer–solvent systems: PS(166000) + cyclohexane PS(51000) + cyclohexane with the upper critical solution temperature (UCST), PE(14300) + n-pentane, and PE(442100) + n-hexane with the lower critical solution temperature (LCST). All the parameters needed in these calculations are listed in Table 10.

From the thermodynamic stability criteria, the spinodal can be derived by solving

$$\left(\frac{\partial^2 G_\phi}{\partial {\phi_1}^2}\right)_{T,P} = 0 \tag{30}$$

and the critical point is determined by the equation

$$\left(\frac{\partial^3 G_\phi}{\partial {\phi_1}^3}\right)_{T,P} = 0 \tag{31}$$

An analytical expression for the first derivative of G_ϕ with respect to the polymer segmental fraction, ϕ_1, for the OCM EOS can be derived. However, the second and third derivatives have been solved by the numerical central difference method, with $\Delta\phi_1 = 10^{-4}$–10^{-5} in our calculations.

To test the accuracy of the numerical method used for the calculation of the derivatives, we calculated the critical temperatures and compositions for the PE(8000), PE(177000), PE(1000000) + n-hexane systems and compared the results with those of Nies et al.[10] Good agreement was obtained and indicates that the derivatives and numerical method used here are correct and reliable.[11]

Table 9. Results for the Activity Calculation of Solvents and the Interaction Parameters for OCM EOS

mixture	temp range (K)	no. of data points	parameters ζ	η	ξ	AAD[a]	data source
PIB + benzene	298.15	11	0.9730	1.2868	0.6367	1.08	24
PIB + cyclohexane	298.15	8	0.9996	0.8563	1.4596	0.39	25
PIB + pentane	298.15–328.15	22	1.0021	0.8446	1.7253	1.63	26
PB + benzene	300.05	8	1.0147	0.9150	1.1801	0.17	27
PEO + benzene	318.95–343.15	14	1.0017	1.1534	0.4632	0.16	21
PO + benzene	320.35–347.85	26	1.0166	0.9152	1.1034	0.47	28
PIB + octane	298.15	5	0.9953	1.0615	1.0475	0.05	29
grand ave						0.56	

[a] $\mathrm{AAD}(U) = (1/N)\sum|U_i^{\mathrm{calc}} - U_i^{\mathrm{exp}}|/U_i^{\mathrm{exp}} \times 100$.

Table 10. Pure Component Molecular Parameters and the Interaction Parameters for OCM EOS

Pure Component Molecular Parameters

component	ϵ^* (MPa·cm^3/mol)	v^* (cm^3/mol)	C_s	β	M_0 (g/mol)
PS	3617.9	50.76	0.333	0.0226	52.6
PE(14300)	3240.4	43.19	0.333	0.2000	37.0
PE(442100)	3242.1	43.19	0.333	0.2000	37.0
cyclohexane	3369.9	55.80	0.561	0.1620	46.8
n-pentane	2250.9	48.89	0.396	0.2000	35.0
n-hexane	2247.6	47.00	0.360	0.2000	34.4

Interaction Parameters

mixture	ζ	η	ξ
PS + cyclohexane[a]	0.9844	1.0570	1.6515
PS + cyclohexane[b]	0.9849	1.0237	1.8956
PE *n*-pentane	0.9855	1.3955	1.0000
PE + *n*-hexane	0.9811	1.3999	1.0000

[a] Molecular weight of PS is 166 000. [b] Molecular weight of PS is 51 000.

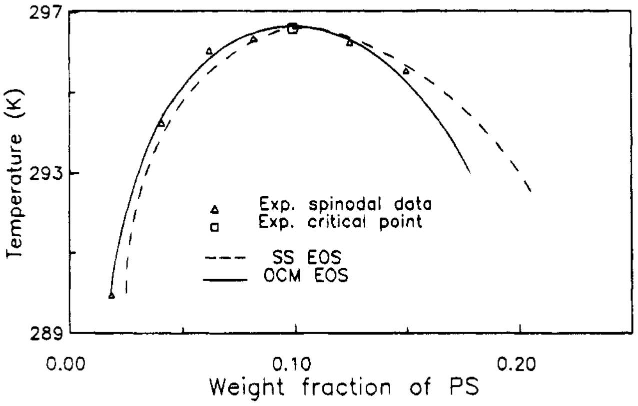

Figure 1. Spinodal curves for the system PS(166000) + cyclohexane.

We have investigated two systems with UCST type curves, PS(166000) + cyclohexane and PS(51000) + cyclohexane. The three parameters for each system are determined by fitting the experimental spinodal and critical point data. Figures 1 and 2 show our calculated and experimental results as well as the results of the SS EOS presented by Stroekes and Nies.[12] As is seen in Figures 1 and 2, only the OCM EOS presents a much better fit to both the solvent-rich and polymer-rich branches, in particular for the PS(51000) + cyclohexane system. This improvement seems partly to be attributed to the introduction of the third binary interaction parameter ξ in our EOS. In conclusion, the OCM EOS can describe the phase diagram with UCST quantitatively, compared with the semiquantitative results of the SS EOS.

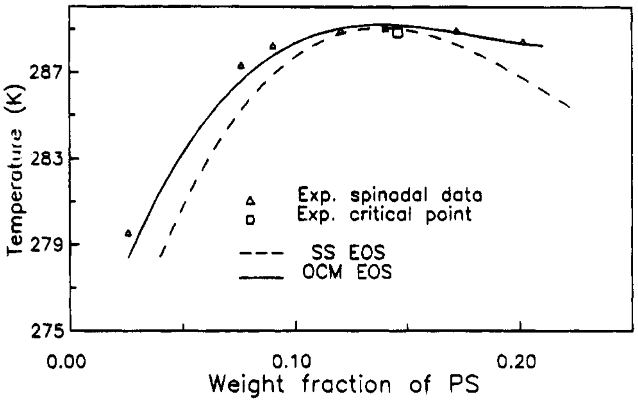

Figure 2. Spinodal curves for the system PS(51000) + cyclohexane.

Many polymer solutions exhibit LCST type phase diagrams. Due to a lack of binodal and spinodal experimental data, we have only used the experimental cloud point data for the PE(14300) + *n*-pentane and PE(442100) + *n*-hexane systems reported by Hamada et al.[13] to test the capability of the OCM EOS in this respect.

First, two critical points, T_c = 382.35 K and ϕ_{1c} = 0.051 for PE(14300) + *n*-pentane and T_c = 414.15 K and ϕ_{1c} = 0.02 for PE(442100) + *n*-hexane, can be solved in terms of the experimental cloud point data. Then two binary interaction parameters ζ and η can be determined from the critical points obtained above, while the third parameter ξ is set to unity. From these parameters (see Table 10), we have calculated a series of data points and plotted the spinodal curves for these two systems in Figures 3 and 4, along with the experimental cloud point curves. The similarity between the shapes of the spinodal and cloud point curves in Figures 3 and 4 indicates that the OCM EOS is, at least, capable of representing the LCST type phase diagrams semiquantitatively.

It should be pointed out that the description of phase behavior discussed here is only applied to model systems with apolar interactions between molecules and/or segments, in which the random mixing concept adopted in the OCM EOS is applicable. However, for the systems with strong directional interactions, e.g., associations, as was addressed by Xie and Nies,[14] nonrandom mixing theory is suited to deal with the phase behavior in a consistent manner. As a result, more parameters for their EOS and more complicated computation are needed.

4. Discussion and Conclusions

The OCM EOS proposed in our preceding paper has been extended to a variety of polymer solutions. To test its capability, the OCM EOS has been used for the estimations of various thermodynamic properties, including *P*–*V*–*T* relations, the excess volumes and

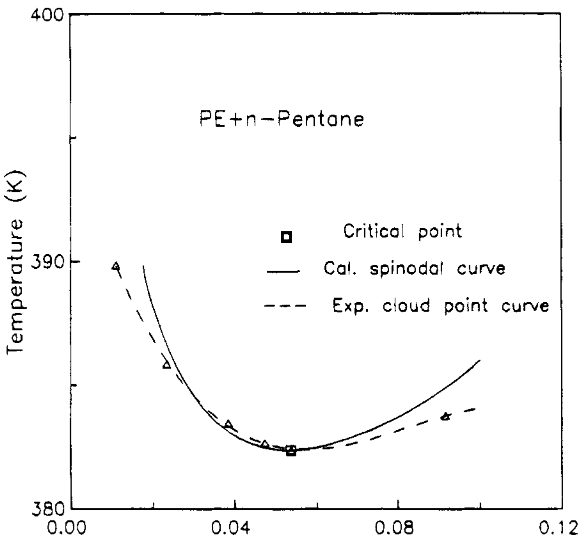

Figure 3. Calculated spinodal curve and experimental cloud point curve for the system PE(14300) + *n*-pentane.

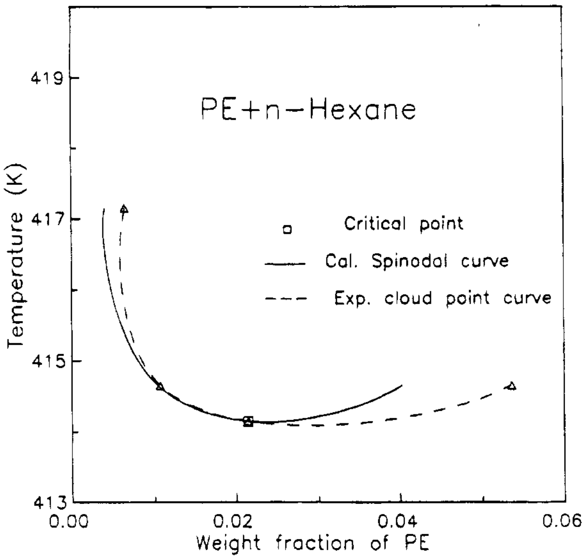

Figure 4. Calculated spinodal curve and experimental cloud point curve for the system PE(442100) + *n*-hexane.

enthalpies, solvent activities, and phase diagrams, for polymer–solvent and blend systems. Compared with the SS EOS, which has been evaluated as one of the best EOSs,[3] the OCM EOS can present better results for $P-V-T$ relations and quantitative description of phase diagrams with the UCST type, in particular. As for the correlation of the excess volume and enthalpy as well as $P-V-T$ for polymer solutions simultaneously, through a careful selection of the binary interaction parameters, reasonable results can be attained within a compromised accuracy tolerance. It should be pointed out, since the so-called spatial structure parameter β's for many substances are set to a constant, the third binary interaction parameter ξ vanishes. As a result, in most cases, only two binary interaction parameters, regressed from the experimental data of the binary systems of interest, are needed in the OCM EOS.

All the calculations in this work indicate that based on the open-cell concept, the OCM EOS proposed in our preceding paper can be applied to not only pure substances but also polymer solutions and blends with satisfactory accuracies. In summary, it is worth noticing that though the hole-cell liquid theory is well developed, there is still some room for improvement, as shown in this work.

Acknowledgment. This work was supported by the National Natural Science Foundation of China and the Doctoral Studies Foundation of Science and Technology, the State Education Commission of China. The authors thank Mr. Huimin Liang for useful discussions and Dr. C. H. Twu for helpful suggestions.

Appendix A. Derivation of the Excess Enthalpy

From the thermodynamic relations $H = U + PV$ and $U = kT^2(\partial \ln Z/\partial T)_{V,N}$, we obtain

$$H = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} + PV \qquad \text{(A-1)}$$

Z is the canonical partition function,

$$Z = \frac{Q}{N!\Lambda^{3Nc}} \qquad \text{(A-2)}$$

where $\Lambda = h/(2\pi mkT)^{1/2}$ and Q is the configurational partition function. Thus

$$\ln Z = \ln Q + \frac{3Nc}{2}\ln T + A \qquad \text{(A-3)}$$

where A represents the summation of all the temperature-independent terms.

For a mixture consisting of N_i molecules

$$H_\phi^{\mathrm{m}} = RT^2\left[\frac{\partial(\ln Z/\sum N_is_i)}{\partial T}\right]_{V,N} + PV_\phi \qquad \text{(A-4)}$$

where H_ϕ^{m} and V_ϕ are the enthalpy and the volume per mole of segment, respectively.

For a mixture, from eq A-3, we get

$$\frac{\ln Z}{\sum N_is_i} = \frac{\ln Q}{\sum N_is_i} + \frac{3}{2}\langle c_s\rangle \ln T + \frac{A}{\sum N_is_i} \qquad \text{(A-5)}$$

For the OCM EOS eq A-5 is written as

$$-\frac{\ln Q}{\sum N_is_i} \propto \frac{\ln y}{\langle s\rangle} + \frac{(1-y)}{y}\ln(1-y) - \langle c_s\rangle\left[\ln\left[\frac{\langle v^*\rangle(1-W)^3}{QQ}\right] + RR - yQQ^2\frac{(1.011QQ^2 - 2.409)}{2\bar{T}}\right] \qquad \text{(A-6)}$$

where

$$QQ = (y\bar{V})^{-1}, \qquad W = 0.8909yQQ^{1/3},$$

$$RR = \ln\left[1 + 10.7\langle\beta\rangle\frac{(1-y)}{y}\exp\left[\frac{0.0052\langle c_s\rangle y}{2\bar{T}(1-y)}\right]\right] \qquad \text{(A-7)}$$

Note that in eqs A-6 and A-7, only the temperature-dependent terms remain.

The derivative can be solved in terms of the difference method:

$$\left[\frac{\partial(\ln Z/\sum N_is_i)}{\partial T}\right]_{V,N} \approx \left(\frac{\Delta(\ln Z/\sum N_is_i)}{\Delta T}\right)_{V,N} \qquad \text{(A-8)}$$

where $\Delta T = 10^{-5}$.

Combining the equations above and eq 27, we obtain $H_\phi{}^m$ for the mixture, the enthalpies for pure components, and, furthermore, the excess enthalpy, $H_\phi{}^E$.

Appendix B. Derivation of $(\partial G_\phi/\partial \phi_1)_{T,P}$

From the thermodynamic relation,

$$G_\phi = A_\phi + PV_\phi \qquad \text{(B-1)}$$

where G_ϕ, A_ϕ, and V_ϕ are the Gibbs free energy, Helmholtz free energy, and volume per mole of segment, respectively.

Therefore,

$$\left(\frac{\partial G_\phi}{\partial \phi_1}\right)_{T,P} = \left(\frac{\partial A_\phi}{\partial \phi_1}\right)_{T,P} + P\left(\frac{\partial V_\phi}{\partial \phi_1}\right)_{T,P} \qquad \text{(B-2)}$$

To solve the two terms on the right side of eq B-2, two derivatives, $(\partial y/\partial \phi_1)_{T,P}$ and $(\partial V/\partial \phi_1)_{T,P}$, are needed. They can be obtained by solving and differentiating eqs 22 and 24 simultaneously. For simplicity, the detailed derivations are omitted here.

References and Notes

(1) Chongli Zhong; Wenchuan Wang; Huanzhang Lu *Macromolecules* **1994**, *27*, 660.
(2) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(3) Jain, R. K.; Simha, R. *Macromolecules* **1980**, *13*, 1501.
(4) Dee, G. T.; Walsh, D. J. *Macromolecules* **1988**, *21*, 811.
(5) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *48*, 1061.
(6) Flory, J. P.; Orwoll, R. A.; Vrij, A. J. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(7) Dee, G. J.; Walsh, D. J. *Macromolecules* **1988**, *21*, 815.
(8) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(9) Renuncio, J. A. R.; Prausnitz, J. M. *Macromolecules* **1976**, *9*, 898.
(10) Nies, A.; Stroeks, R.; Simha, R.; Jain, R. K. *Colloid Polym. Sci.* **1990**, *268*, 731.
(11) Zhong, C. Ph.D. Thesis, Beijing Institute of Chemical Technology, China, 1993.
(12) Stroeks, A.; Nies, E. *Polym. Eng. Sci.* **1988**, *28*, 1347.
(13) Hamada, F.; et al. *Polym. J.* **1973**, *4*, 316.
(14) Xie, H.; Nies, E. *Macromolecules* **1993**, *26*, 1689.
(15) Beret, S.; Prausnitz, J. M. *Macromolecules* **1975**, *8*, 536.
(16) Zoller, P.; Hoehn, H. H. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1385.
(17) Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*; Hemisphere Publishing Corp.: Washington, 1975.
(18) Jonas, J.; Hasha, D.; Huang, S. G. *J. Phys. Chem.* **1980**, *84*, 109.
(19) Lichtenthaler, R. N.; et al. *Macromolecules* **1977**, *11*, 192.
(20) Barlow, J. W. *Polym. Eng. Sci.* **1978**, *18*, 238.
(21) Booth, C.; Devoy, C. J. *Polymer* **1971**, *12*, 309.
(22) Lakhanpal, M. L.; Conway, B. E. *J. Polym. Sci.* **1960**, *66*, 75.
(23) Boelhouwer, J. W. M. *Physica* **1960**, *66*, 1021.
(24) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2053.
(25) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2061.
(26) Baker, C. H.; Brown, W. B.; et al. *Polymer* **1962**, *3*, 215.
(27) Jessup, R. S. *J. Res. Natl. Bur. Stand.* **1958**, *60*, 2820.
(28) Booth, C.; Devoy, C. J. *Polymer* **1971**, *12*, 320.
(29) Flory, P. J.; Ellenson, J. L.; Eichinger, B. E. *Macromolecules* **1968**, *1*, 279.

MA946399R