Macromolecules **1984**, *17*, 2663–2668 **2663**

(16) Pennings, A. J. *J. Polym. Sci., Part C* **1967**, *16*, 1799.
(17) Salovey, R.; Hellman, M. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 647.
(18) Flory, P. J. "Principles of Polymer Chemistry", Cornell University Press: Ithaca, NY, 1953.
(19) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *A234*, 60.
(20) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci., Part A-3* **1968**, *6*, 325.

Statistical Thermodynamics of Multicomponent Fluids. 2. Equation of State and Phase Relations

R. K. Jain and Robert Simha*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. *Received February 27, 1984*

ABSTRACT: The theory previously formulated for the equation of state (*PVT*) is now extended to the free energy change ΔG_m by including the requisite additional contributions to the free energies of components and mixtures. As an example of a compatible binary mixture with experimentally known *PVT* and chemical potentials, we consider the *n*-hexane + *n*-hexadecane pair. The former data set had previously been discussed in terms of the theory. Without introduction of additional parameters, both sets of properties are quantitatively described. The very minor corrections in the scaling pressure arise from two facts. First, this parameter is predicted by the theory without adjustment to pressure data of the mixture, and second, ΔG_m is computed as a difference between large quantities. This correction leaves the predicted equation of state practically unaltered. General procedures for the combined analysis of chemical potentials and *PVT* are outlined. As an example of a polymer solution we consider the polyethylene + *n*-hexane pair for a low (M = 8000) and high (M = 177 000) uniform molecular weight. The equation of state of both components and thus their scaling parameters are known, but sufficient information for the mixture is not available, to define the corresponding parameters. Here a relative cross-interaction parameter becomes the important quantity to be explored. Lower critical solution temperatures (T_c) and cloud point curves are computed. Small variations in the above parameters within the bounds suggested by the equation of state analysis of the C_6 + C_{16} pair have a significant effect on T_c. In view of the success of the equation of state it is of interest to examine the effect of pressure. The computed increments of T_c conform to an iso-free volume difference condition, where free volume is defined in terms of the hole fraction inherent in the theory. Similarly a reduced cloud point curve can be established.

I. Introduction

We have recently extended the particular version of statistical theory for a homogeneous melt to multicomponent systems.[1] The specific applications were to the equation of state of low[1] and high molecular weight[2] blends. The essential consequence of this extension is the view of the mixture as a homogeneous system with explicitly composition-dependent parameters. The dependence of the scaling parameters of pressure, volume, and temperature in particular involves self- and cross-segmental attractive and repulsive interactions. A particular result is the prediction of the scaling pressure without further recourse in principle to pressure experimentation required.

The theory has shown quantitative success for a variety of fluids and their mixtures in respect to the volume derivative of the free energy. This implies that the characteristic parameters, extracted from extensive comparisons with *PVT* experiments at low and elevated pressures, are to be regarded as true constants of the system at fixed composition. No variations with temperature or pressure are permitted to generate acceptable concordance between theory and experiment. Admittedly, this agreement is obtained at the minor price inherent in the model, of *evaluating numerically transcendental equations.*

Having gone this far, the purpose of this paper is to explore the position and *some* results of the model in respect to compositional derivatives of the free energy. Chemical potentials are to be computed under single- and two-phase conditions, arising from the existence of lower critical solution temperatures (LCST). As in the instance of the equation of state, we begin with a low molecular weight mixture. Extensive experimental information exists, albeit for free energies of mixing at atmospheric pressure only. The equation of state and thus volume changes ΔV_m have been previously analyzed in theoretical terms at atmospheric and elevated pressures. We continue with an illustration of a polymer solution at low and slightly elevated pressures. Here equation of state data for the components, but not for the mixture, are available. Hence we investigate the influence of variations in certain interaction parameters, guided for reasonable magnitudes by the results for a low molecular weight analogue. A basic question concerns the characteristic parameters. Is the set derived from equation of state data adequate for a description of compositional derivatives, or if corrections have to be introduced, what is their origin and magnitude?

Starting with the early work of Prigogine and his collaborators on chain-molecular fluids, there have been several theoretical approaches connecting equation of state and free energy of mixing. We emphasize that the purpose here is not detailed comparison of our theory with earlier theories. Our concern in this first evaluation of extended theory is to make a detailed comparison with experiment in one case and to illustrate quantitative reasonableness and make some comparison in another.

II. Theory

The molar Helmholtz free energy F_i of component i equals[3]

$$F_i/RT = \ln (y/s_i) + s_i y^{-1}(1 - y) \ln (1 - y) - (s_i - 1) \ln [(z - 1)/e] - 3c_i\{\ln [(M_{0i}V_i{}^*/N_A)^{1/3}(y\tilde{V})^{1/3}(1 - \eta)(2\pi M_{0i}kT/N_A h^2)^{1/2}] - (y/6\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 2.409]\} \quad (1)$$

with

$$\eta = 2^{-1/6}y(y\tilde{V})^{-1/3}$$

0024-9297/84/2217-2663$01.50/0

Table I
Scaling Parameters, Free Energy ΔG_m, and Chemical Potential $\Delta\mu_1$: $x_1 n\text{-}C_6 + x_2 n\text{-}C_{16}$

				T = 293.15 K						T = 333.15 K			
	$\langle V^* \rangle$,[a]	$\langle T^* \rangle$,[a]	$\langle P^* \rangle$,[a]	$-\Delta G_m/RT$		$\langle P^* \rangle$(adj),[c]	$-\Delta G_m/RT$(adj)	$-\Delta\mu_1/RT$		$-\Delta G_m/RT$		$-\Delta\mu_1/RT$	
x_1	cm^3/g	K	bar	theory	expt[b]	bar	theory[c]	theory[c]	expt[b]	theory[e]	expt[b]	theory	expt[b]
0	1.2090	7448	6785										
0.2	1.2134	7131	6813	0.399	0.518	6825	0.515	1.62	1.68	0.521	0.521	1.50	1.69
0.4	1.2222	6799	6878	0.707	0.699	6878	0.707	0.98	0.95	0.701	0.702	0.91	0.96
0.5	1.2289[d]	6626[d]	6930[d]	0.881	0.720	6909	0.719	0.73	0.72	0.698	0.723	0.68	0.72
0.6	1.2362	6433	6993	0.997	0.698	6951	0.698	0.52	0.53	0.664	0.702	0.49	0.53
0.8	1.2509	5895	7088	0.706	0.517	7056	0.519	0.24	0.23	0.500	0.519	0.24	0.23
1.0	1.2763	5197	7201										

[a] From ref 1. [b] Ref 4. [c] See text. [d] Interpolated parameters. [e] Using $\langle P^* \rangle$ from column 7.

Here, M_{0i} is the molecular weight of the segment and v_i^* its repulsive volume, with $V_i^* = N_A v_i^*/M_{0i}$, the corresponding specific volume. It will be noted that the free energy, eq 1, contains terms which are independent of y, the fraction of occupied sites in the quasi-lattice, and hence could be ignored in the computation of the pressure $P = -(\partial F/\partial V)_T$. The scaling parameters V_i^*, T_i^*, and P_i^* are derived from the scaled equation of state:[3]

$$\tilde{P}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045] \tag{2}$$

The "excess" free volume fraction $h = 1 - y$ satisfies the conditional relation

$$(s_i/3c_i)[(s_i - 1)/s_i + y^{-1}\ln(1-y)] = (1-\eta)^{-1}(\eta - 1/3) + (y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}] \tag{3}$$

$3c_i/s_i$ is the flexibility parameter, i.e., the number of effectively external degrees of freedom per segment of the s_i-mer.[1-3]

The scaling parameters for the components are defined as follows:

$$P_i^* = q_i z \epsilon_i^*/s_i v_i^*$$
$$T_i^* = q_i z \epsilon_i^*/c_i k \tag{4}$$

Here, $q_i z = s_i(z-2) + 2$, and $z = 12$ is the coordination number; ϵ_i^* represents the maximum attraction energy between a pair of i-type segments. The corresponding equations for the binary mixture of specified molar composition $x_1 = x = 1 - x_2$ involve the weight average $\langle M_0 \rangle$, the number averages $\langle s \rangle$ and $\langle c \rangle$, and the averages $\langle V^* \rangle$, $\langle P^* \rangle$, $\langle T^* \rangle$ defined in accordance with eq 4. For simplicity we omit henceforth the brackets. The following relations obtain:

$$\epsilon^* v^{*2} = X_1^2\epsilon_{11}^* v_1^{*2} + 2X_1X_2\epsilon_{12}^* v_{12}^{*2} + X_2^2\epsilon_{22}^* v_2^{*2}$$
$$\epsilon^* v^{*4} = X_1^2\epsilon_{11}^* v_1^{*4} + 2X_1X_2\epsilon_{12}^* v_{12}^{*4} + X_2^2\epsilon_{22}^* v_2^{*4} \tag{5}$$

with X_i representing site fractions equal to $x_i q_i/\sum x_i q_i$. The parameters appearing above are related by the equation

$$P^*V^*/T^* = R(c/s)M_0^{-1} \tag{6}$$

with the corresponding expressions for each of the components. Since the right-hand side is entirely defined by the properties of the components, P^* can indeed be computed once V^* and T^* have been determined by a superposition of the experimental and the reduced theoretical atmospheric pressure ($\tilde{P} \simeq 0$) isobar. The assumption adopted in our earlier work for chain-molecular components and hence also the blend is $3c/(s+3) = 1$.

The molar Helmholtz free energy F_m of the binary mixture equals[1]

$$F_m/RT = x_1\ln x_1 + x_2\ln x_2 - (s-1)\ln[(z-1)/e] + \ln(y/s) + sy^{-1}(1-y)\ln(1-y) - 3c\{\ln[(M_0V^*/N_A)^{1/3}(y\tilde{V})^{1/3}(1-\eta)(2\pi M_0kT/N_Ah^2)^{1/2}] - (y/6\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 2.409]\} \tag{7}$$

The chemical potentials of the mixture can be formally obtained by appropriate differentiation of eq 7. This involves the derivatives of ϵ^*, v^*, and y with respect to composition and consequently results in cumbersome manipulations. It is more convenient to employ alternative expressions for the changes $\Delta\mu_i$ of the chemical potentials, viz.

$$\Delta\mu_1 = \Delta G_m - x_2\left(\frac{\partial\Delta G_m}{\partial x_2}\right)_{P,T}$$
$$\Delta\mu_2 = \Delta G_m + x_1\left(\frac{\partial\Delta G_m}{\partial x_2}\right)_{P,T} \tag{8}$$

with $\Delta G_m = G_m - xG_1 - (1-x)G_2$. The G functions are derived from eq 1-3, eq 7, and their analogues. In what follows accurate polynomials will be fitted to the theoretical expressions, following from eq 7 and 1-3, as functions of composition at a given temperature and pressure.

III. *n*-Hexane + *n*-Hexadecane Pair

We have discussed the equation of state of the components and their blends[1] over an extensive range of variables. Thus the scaling parameters are known. Detailed measurements of the activities provide the chemical potentials and free energy of mixing at atmospheric pressure.[4] The experimental results are summarized in the form of polynomials for the excess over the respective quantities for the ideal mixture.

As indicated in section II we will approximate the theoretical expressions for $\Delta G_m = \Delta F_m + P\Delta V_m$ by polynomials in order to obtain $\Delta\mu$ from eq 8 in a convenient way. Application of eq 1-3, 7, and 8 employing the scaling parameters from ref 1 and listed in Table I, yields the results for ΔG_m seen in column 5 therein. Throughout, ΔG_m is defined as the difference $G_m - x_1G_1 - x_2G_2$. To the original parameter values given in ref 1 we have added the additional point $x = 0.5$. Significant deviations from measurements given in column 6 are noted, which would be magnified in respect to the chemical potentials. Are these departures due to inherent weakness in the theory propounded, which may be quantitatively adequate with respect to the volume derivatives of the partition function but faulty with regard to compositional derivatives? Or could it be that the theory has not been properly applied?

To explore this point we note that the scaling pressure $\langle P^* \rangle$ for the mixtures is *not* derived by superposition of

Table II
Characteristic Parameters: $x_1 n\text{-C}_6 + x_2\text{PE}$ (M_2 = 8000)

				ϵ_{12}^*/k = 352.9				ϵ_{12}^*/k = 360.0			
$x_2 \times 10^4$	w_2, %	$\langle s\rangle$	$\langle 3c\rangle/\langle s\rangle$	$\langle\epsilon^*\rangle/k$, K	$\langle V^*\rangle$, cm^3/g	$\langle T^*\rangle$, K	$\langle P^*\rangle$, bar	$\langle\epsilon^*\rangle/k$, K	$\langle V^*\rangle$, cm^3/g	$\langle T^*\rangle$, K	$\langle P^*\rangle$, bar
0	0	2.500	2.200	352.90	1.2763	5197.0	7201.4	352.90	1.2763	5197.0	7201.4
1	0.920	2.525	2.188	352.70	1.2758	5218.7	7201.3	352.83	1.2757	5220.6	7204.1
2	1.823	2.550	2.177	352.51	1.2751	5239.9	7201.6	352.76	1.2750	5243.6	7207.0
3	2.710	2.575	2.165	352.31	1.2744	5260.9	7201.9	352.68	1.2743	5266.4	7209.8
4	3.582	2.600	2.154	352.12	1.2737	5281.7	7202.1	352.60	1.2736	5288.9	7212.6
5	4.438	2.625	2.143	351.93	1.2731	5302.3	7202.3	352.52	1.2729	5311.1	7215.3
6	5.279	2.650	2.132	351.74	1.2724	5322.6	7202.6	352.44	1.2723	5333.2	7217.8
7	6.106	2.675	2.122	351.55	1.2718	5342.8	7202.8	352.35	1.2716	5354.9	7220.3
8	6.918	2.700	2.111	351.37	1.2712	5362.8	7203.0	352.27	1.2709	5376.5	7222.7
9	7.717	2.725	2.101	351.18	1.2705	5382.5	7203.3	352.18	1.2703	5397.8	7225.0
10	8.502	2.750	2.091	351.00	1.2699	5402.1	7203.5	352.09	1.2696	5418.8	7227.3
1×10^4	100	252.2	1.012	325.70	1.1417	9772.0	7566.1	325.70	1.1417	9772.0	7566.1

experimental and theoretical isotherms but *predicted* from eq 6. The results exhibited in ref 1 represent satisfactory predictions of the volume at pressures of maximally 4.5 kbar. As for the prediction of free energies from the equation of state, the scaling pressure must be known even at low pressures ($\tilde{P} \rightarrow 0$). Since energy is scaled by the product P^*V^* in the equation of state contributions to F, one anticipates that the effect of even miniscule variations in numerical values on the free energy ΔF_m, a small difference between three large quantities, will be profound. It should also be noted in this connection that in the fitting of elevated pressure isotherms for the components, the P_i^* are subject to small fluctuations. These arise in oligomers from the definition of the average segment.

In view of the above it is reasonable to enquire what adjustments in the single parameter $\langle P^*\rangle$ are required to generate coincidence between experiment and prediction. Thus quantities $\langle P^*\rangle$(adj) are derived by means of the equation

$$\langle P^*\rangle(\text{adj})/\langle P^*\rangle = (\Delta G_\text{m} + x_1G_1 + x_2G_2)/(\Delta G_\text{m}(\text{exptl}) + x_1G_1 + x_2G_2) \quad (9)$$

The result is seen in column 7 of Table I. It is not meaningful to use more than four places in $\langle P^*\rangle$. Hence the recomputed ΔG_m in the above equation differ slightly from the original input; compare columns 6 and 8. In any case the differences between the $\langle P^*\rangle$ and $\langle P^*\rangle$(adj), column 7, are insignificant indeed and would *not* affect the equation of state. To obtain finally the chemical potential difference $\Delta\mu_1$, we find it convenient to approximate the computed free energies by a second-order polynomial in x, since the variation in ΔG_m over the whole range of compositions is small. This polynomial yields a maximum error of 1% and a root-mean-square departure of 0.17%. The resulting $\Delta\mu$ values compare well with the experimental data. Consider next the upper limit of temperature, 333.15 K, investigated by McGlashan and Williamson.[4] Table I again contains the pertinent comparisons, obtained with the aid of the scaling pressure $\langle P^*\rangle$ at the lower temperature. Once more a satisfactory agreement obtains.

We conclude that the theory is in principle capable of describing both the equation of state and the configurational free energy of the blend under single-phase conditions. In practice one will extract the scaling quantities of volume, and temperature from the atmospheric pressure isobar, and the scaling pressure of the blend from free energy data. The latter can be determined by means of activity measurements as in the instance of ref 4. To proceed, one will employ eq 6 to obtain a first approximate set of $\langle P^*\rangle$ values for all compositions, recalling that $\langle M_0\rangle$ is a weight average, while $\langle c\rangle$ and $\langle s\rangle$ are number averages.[1] Equation 9 then will serve to derive an improved set, if required.

We could proceed with the prediction of pressure effects but dispense with this. As far as we know, detailed experimental information for the $n\text{-C}_6 + n\text{-C}_{16}$ pair is not available. On the basis of the performance of the theoretical equation of state in the case of other low molecular weight pairs,[1] one expects for these results similar to those seen here. It would be of particular interest to examine the behavior of other hydrocarbon blends, which have been the objects of attention by other investigators.[5-7]

IV. Polymer Solutions: LCST and Phase Equilibria

To probe the position of the theory, we proceed in a manner different from that for the previous blends where the scaling parameters had already been established.[1] Here we investigate the effect of cross interactions and of pressure on the phase relations. As a corollary, the behavior of the characteristic free volume fractions h_1 and h_2 of the components and the possible existence of corresponding state relations will be examined. We have selected polyethylene in n-hexane as a test case. This particular choice is suggested by practical considerations as well as convenience, since the equations of state of the solvent and polymer have been studied in detail.[1,8]

As in the preceding section, the theoretical values of ΔG_m are to be approximated by polynomials in the evaluation of chemical potentials and their derivatives. The larger changes in ΔG_m require higher than second-degree polynomials. We find quartics to be adequate for the present purposes. Thus one has with x_2 the mole fraction of polymer component 2:

$$\Delta G_\text{m} = \sum_0^4 a_i x_2^{\,i}$$

$$\Delta\mu_1 = \Delta G_\text{m} - x_2(\partial\Delta G_\text{m}/\partial x_2) = -\sum_0^4 (i-1)a_i x_2^{\,i}$$

The further derivatives are

$$\partial\Delta\mu_1/\partial x_2 = -\sum_2^4 i(i-1)a_i x_2^{\,i-1}$$

$$\partial^2\Delta\mu_1/\partial x_2^2 = -\sum_2^4 i(i-1)^2 a_i x_2^{\,i-2}$$

The critical composition x_c is defined by the vanishing of the last two derivatives. This requires the following relations between the coefficients a_i and x_c:

$$x_\text{c} = -a_3/(4a_4) \equiv -(2/3)a_2/a_3 \equiv [a_2/(6a_4)]^{1/2}$$

$$a_3^2 \equiv (8/3)a_2a_4 \quad (10)$$

Table III
Free Energy Changes $-(\Delta G_m/RT) \times 10^3$ for n-Hexane + Polyethylene at P = 1 bar, M_2 = 8000

	ϵ_{12}^*/k = 352.9 K						ϵ_{12}^*/k = 360.0 K					
	T = 420 K		T = 430 K		T = 440 K		T = 450 K		T = 472 K		T = 485 K	
$x_2 \times 10^4$	theory	quartic	theory	quartic	theory	quartic	theory	quartic	theory	quartic	theory	quartic
1	2.645	2.633	2.466	2.458	2.275	2.272	5.375	5.372	4.560	4.559	4.052	4.050
2	4.426	4.437	4.099	4.108	3.758	3.759	9.975	9.977	8.425	8.424	7.444	7.447
3	6.161	6.183	5.699	5.712	5.198	5.209	14.509	14.523	12.244	12.255	10.822	10.828
4	7.916	7.898	7.310	7.292	6.657	6.640	19.039	19.029	16.080	16.067	14.216	14.206
5	9.616	9.601	8.866	8.862	8.064	8.066	23.516	23.507	19.868	19.872	17.591	17.590
6	11.314	11.301	10.432	10.430	9.489	9.493	27.969	27.962	23.681	23.676	20.984	20.984
7	12.996	12.998	11.997	11.996	10.929	10.923	32.395	32.398	27.482	27.479	24.387	24.390
8	14.670	14.683	13.553	13.554	12.354	12.353	36.796	36.808	31.273	31.278	27.804	27.804
9	16.304	16.336	15.066	15.089	13.759	13.773	41.177	41.185	35.054	35.063	31.219	31.222
10	17.956	17.930	16.596	16.580	15.175	15.167	45.522	45.512	38.827	38.820	34.635	34.632

Table IV
Critical Composition x_c and Polynomial Coefficients

P, bar	T_c, K	$10^4 x_c$, eq 10			$10^3 a_3$	$10^3 \times (8a_2a_4/3)^{1/2}$
		$-a_3/4a_4$	$-2a_2/3a_3$	$(a_2/6a_4)^{1/2}$		
			ϵ_{12}^*/k = 352.9 K			
1	430	5.54	5.54	5.54	6.795	6.798
50	445	5.71	5.68	5.70	6.724	6.745
100	460	5.69	5.70	5.69	6.406	6.413
			ϵ_{12}^*/k = 360.0 K			
1	472	5.68	5.65	5.67	4.874	4.863
50	495	5.87	5.88	5.88	3.776	3.780
100	516	5.74	5.71	5.72	5.035	5.019

Hence sign a_2 = sign a_4, and sign a_3 = $-$sign a_2.

In Table II the numerical values of the requisite parameters are displayed. Equation 5 yields $\langle\epsilon^*\rangle$ and $\langle v^*\rangle$ for a given x_2, v_i^* and ϵ_{ii}^*, i = 1, 2. Moreover, ϵ_{12}^* and v_{12}^* must be known. In the n-C$_6$ + n-C$_{16}$ pair some variation of ϵ_{12}^* and v_{12}^* with composition has been noted.[1] We are guided by these results in selecting two values for the ratio $\epsilon_{12}^*/\epsilon_{11}^*$, namely, 1 and 1.02. The repulsion parameter v_{12}^* is taken as the average $\{[(v_1^*)^{1/3} + (v_2^*)^{1/3}]/2\}^3$. The quantities v_2^* and ϵ_{22}^* are known from ref 8. We begin with a low molecular weight of the polymer, viz., M_2 = 8000, or s_2 = 252.2.[8] The compositions evaluated encompass the range shown for example by Kleintjens and Koningsveld[9] for this pair, albeit with a different molecular weight and of course, molecular weight distribution. More is to be said about this below. Over this range, only moderate variations in the scaling parameters of the mixtures occur, and hence additional decimal places are exhibited. This also serves to illustrate the effect of variations in $\epsilon_{12}^*/\epsilon_{11}^*$. The pressure parameter $\langle P^*\rangle$ is proportional to the ratio $\langle\epsilon^*\rangle/\langle v^*\rangle$ and the difference between the two sets is enhanced by the smaller $\langle\epsilon^*\rangle$ and larger $\langle v^*\rangle$ for the first set; see columns 5 and 6 vs. columns 9 and 10.

The range of temperatures to be explored is again suggested by the results in ref 9–11. Table III summarizes the free energies at atmospheric pressure and their polynomial representations. A computer program, SLA-74-0270 developed at Sandia Laboratories by Shampine, Davenport, and Huddleston, was employed to fit $-\Delta G_m/RT$ as a function of x_2 over the range $0.5 \leq x_2 \times 10^4 \leq 10$ and to obtain the derivatives. The maximum deviation in $-\Delta G_m/RT$ is 0.5% but in most cases the residual error is much less than the maximum. This is adequate for our purposes and no systematic efforts were made to further improve the fits by means of other numerical procedures. Moreover, the simplicity of a quartic for the identification of the critical temperature–composition region is evident.

The identical procedure has been employed to compute the thermodynamic functions at P = 50 and 100 bar in the vicinity of the critical temperature. The accuracy of the polynomials is about identical with what has been seen in Table III. The maximum residual errors vary between 0.05 and 0.3% in ΔG_m. The whole picture of course is displaced to higher temperatures.

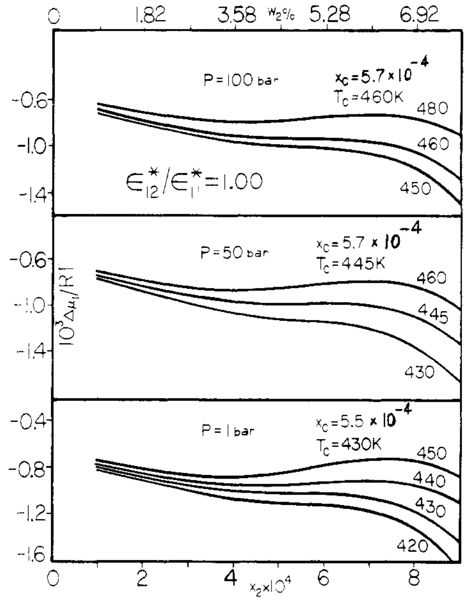

Figure 1. Chemical potential as a function of polymer concentration for a series of temperatures and pressures; $\epsilon_{12}^* = \epsilon_{11}^*$.

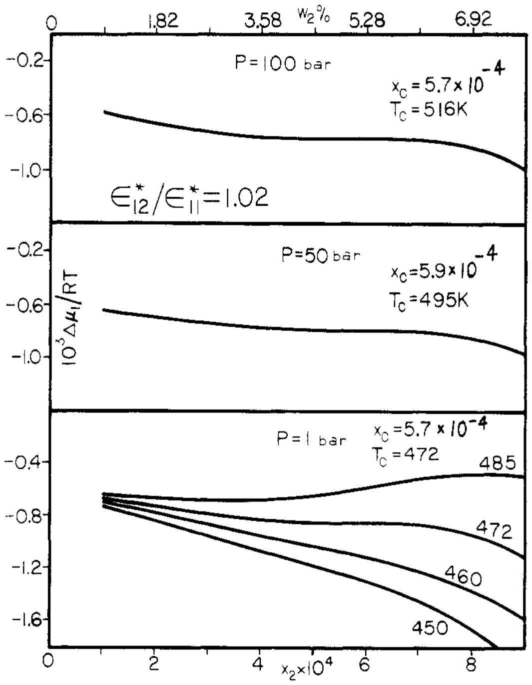

Figure 2. Chemical potential as a function of polymer concentration for a series of temperatures and pressures; $\epsilon_{12}^* = 1.02\epsilon_{11}^*$.

Table V
Critical Coordinates: *n*-Hexane + Polyethylene

M_2	LCST, °C obsd	LCST, °C calcd	$\mathrm{d}T_c/\mathrm{d}P$,[a] K/bar	Δh- $(T = T_c)$[a]	$w_2(T = T_c)$, % obsd	$w_2(T = T_c)$, % calcd
8000	150[g]	157[a]	0.30	0.21		4.9
177000	127,[b] 135,[c] 133,[d] 145[e]	70,[c] 91,[f] 126[a]	0.18	0.18	~2,[e] ~1[c]	3.4

[a] This work, $\epsilon_{12}^* = \epsilon_{11}^*$. [b] Reference 17, $M_2 \sim 10^6$. [c] Reference 5, $M_2 = 1.8 \times 10^5$. [d] Reference 11, M_2 extrapolated to infinity. [e] Reference 9, $M_w = 1.77 \times 10^5$. [f] Reference 6. [g] Reference 18, $M_v = 28\,000$.

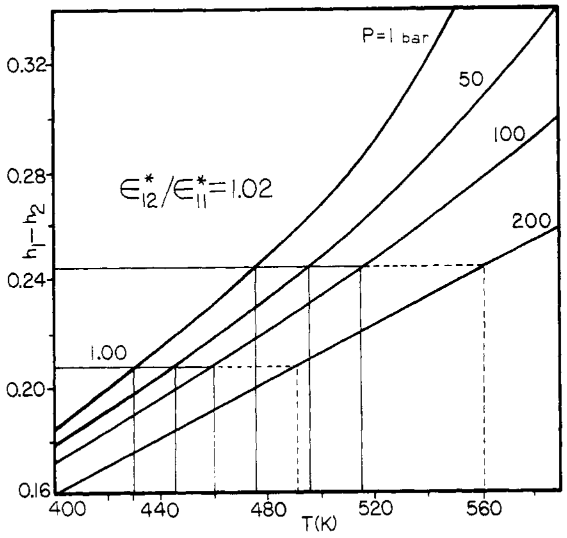

Figure 3. Fractional free volume difference $h_1 - h_2$, eq 3, as a function of temperature from atmospheric pressure to 200 bar. Guide lines indicate location of T_c's. Dashed lines, extrapolated values for 200 bar and two values of $\epsilon_{12}^*/\epsilon_{11}^*$. $M_2 = 8000$.

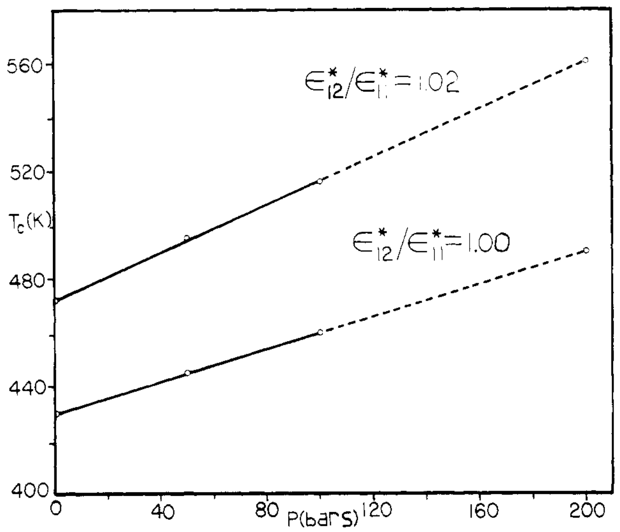

Figure 4. Critical solution temperature as a function of pressure. Dashed lines, extrapolation.

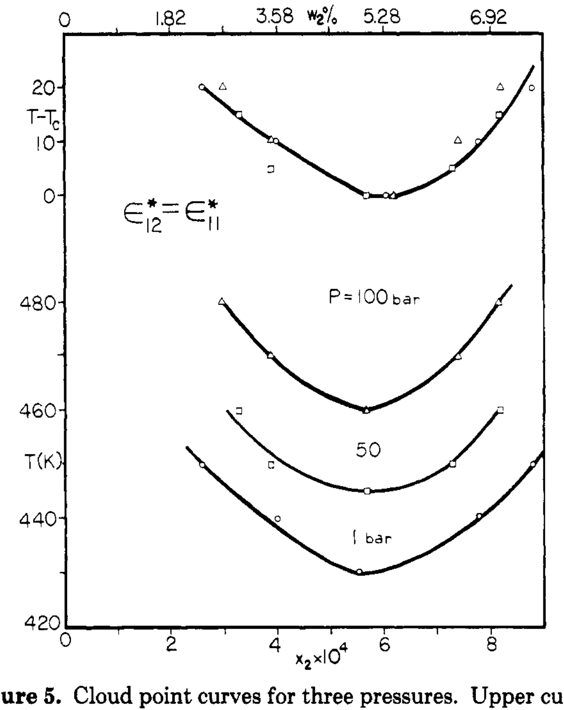

Figure 5. Cloud point curves for three pressures. Upper curve, reduced representation. $M_2 = 8000$.

The chemical potential difference $\Delta\mu_1$ is plotted in Figures 1 and 2 as a function of composition for several temperatures and pressures. Lower critical solution temperatures can be seen. The critical isotherms so marked satisfy eq 10. This is evident from Table IV in which the coefficients a_3 at T_c have been compared with the results from eq 10. Three values of critical concentrations x_c obtained from the identities are in close agreement. Thus the adopted procedure provides consistent results for T_c and x_c.

Next, analogous computations were performed for a uniform molecular weight of 177 000, corresponding to the weight average of polyethylene employed by Kleintjens and Koningsveld.[9] Some results for the two molecular weights are summarized in Table V and will be further considered in what follows.

The critical temperature T_c is seen to increase significantly with increasing pressure and also with an even slight increase in cross-interaction. The latter results in the change of scaling parameters as discussed earlier. The critical compositions x_c, however, exhibit hardly any change; see Table IV. The former two trends as well as the reduction in T_c with increasing molecular weight are readily understood in terms of free volume arguments. The role of free volume quantities in LCST's has been frequently discussed in the literature.[6,10,12] Here we can proceed quantitatively by computing the excess functions $h_1 = 1 - y_1$ and $h_2 = 1 - y_2$ for the components as functions of temperature and pressure. Figure 3 shows the difference $h_1 - h_2$ of solvent and polymer. Universal values of 0.21 and 0.24 respectively obtain and determine the increases of the LCST with increasing pressure and interaction parameter ϵ_{12}^*. An extension of the isobars in Figure 3 results in estimated T_c's equal to 491 and 561 K at P = 200 bar. The pressure coefficients $\mathrm{d}T_c/\mathrm{d}P$ derived from Figure 4 are 0.30 and 0.42 K bar^{-1}. For the higher molecular weight, the characteristic value of the free volume difference is reduced (see Table V), in accord with the lower T_c. Similarly, there is a reduction of the computed pressure coefficient of T_c.

The cloud point curves are obtained by first computing $\Delta\mu_2 = \Delta G_m + x_1(\partial\Delta G_m/\partial x_2)$. $\Delta\mu_1$ and $\Delta\mu_2$ are then plotted as functions of composition and the two equilibrium compositions are determined graphically at each temperature. The results are seen in Figure 5 for $\epsilon_{12}^* = \epsilon_{11}^*$ and the three pressures.

It is of interest to compare these results in a corresponding state manner. In Figure 5 the temperature differences $T - T_c$ are plotted as functions of the equilibrium compositions. Within the scatter possibly resulting from the procedure employed in locating the cloud point curves, a universal representation appears to be valid.

V. Discussion

The theory formulated for one-component and multicomponent systems yields quantitative descriptions of both volume and compositional derivatives of the free energy. This is illustrated by the blends of n-C_6 and n-C_{16}. No additional parameters beyond those already appearing in the equation of state are introduced. The scaling pressure is predicted from equation of state information for mixture and components, as indicated previously.[1] The reasons for the appearance of very small correction factors to this parameter have been discussed. Analogous analyses of polymer solutions require the results of dilatometric measurements for the mixture. In the absence of such detailed information, illustrative computations for the n-hexane + polyethylene pair show the sensitivity of the LCST to slight variations in the segmental cross-interaction and to pressure differences. Whereas the free energy contribution to the equation of state can be scaled, this does not apply to the free energy function F_m; see eq 7. However, one observes certain general relations involving the critical temperature, a corresponding critical free volume difference $h_1 - h_2$ between the two components, and the cloud point curves. Two widely differing molecular weights have been considered but the effects of polydispersity remained to be investigated. As far as we can see, however, no simple average or ratio of averages seems to evolve from the free energy expression.

The particular polymer solution explored here has been the object of several experimental and theoretical studies.[5,6,9-11] The advantage of this selection from our point of view has been the availability of *PVT* information for the components and, as far as the mixture is concerned, of corresponding information at least for an oligomeric analogue of the polymer. The disadvantage for purposes of comparison with experiment is the pronounced polydispersity of polyethylene. Hence with the experimental information at hand and the general theoretical limitations imposed by the assumption of a homodisperse solute, we can do no more here than scan the various threshold temperatures reported in the literature, as seen in Table V. It is to be understood then that the observed values are not to be taken as true T_c's or critical compositions. We have added the computed pressure coefficients of T_c and the free volume differences at the critical temperature.

Where feasible, our approach relies on equation of state information—this for the components at low and elevated pressures, as well as for the mixture, at least at atmospheric pressure. A verification of the numerical value of the predicted scaling pressure or (small) corrections to it[14] will require some input from other excess thermodynamic functions, such as free energy or enthalpy, unless some valid simplifying assumptions emerge. It is these functions or their temperature coefficients which play a paramount role in other theoretical approaches.

A quantity of particular importance in discussing compatibility of polymer blends is the χ parameter. This function is implicitly contained of course in our free energy function. Its dependence on molecular weight, composition, temperature, pressure, and interaction parameters remains to be made explicit.

We still have to investigate polymer blends in the frame of our theory. Equation of state data for a number of polymers of widely varying structures have been discussed over the years by Zoller[15] and us.[2,8,16] Moreover, some enthalpies of mixing are available. They could be combined with the *PVT* information along the lines pursued for the low molecular weight pair. As for model computations, it is suggestive to examine the influence of the characteristic ratio $\epsilon_{12}^*/\epsilon_{11}^*$. Can one in this manner simulate the introduction of small numbers of specific interaction sites, for example through copolymerization, without, by assumption, changing significantly the original scaling parameters of the unmodified components? An extension of the theory to copolymers is another direction to be followed.

Acknowledgment. We are indebted to Professor R. Koningsveld for helpful discussions. This work was supported by the National Science Foundation through Grants DMR 80-12232, and DMR 84-08341, Polymers Program. R.K.J. is on leave from Rajdhani College, University of Delhi, New Delhi 110015, India.

References and Notes

(1) Jain, R. K.; Simha, R. *Macromolecules* **1980**, *13*, 1501. (Note the following misprint in this reference: The term $(1/2)\sum N_i$ in the last line of eq 12 should be replaced by $Ny/2$. Also, the term $(1/3)\ln\langle v^*\rangle$ in the third line of this equation is unnecessary.)
(2) Jain, R. K.; Simha, R.; Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1399.
(3) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(4) McGlashan, M. L.; Williamson, A. G. *Trans. Faraday Soc.* **1961**, *57*, 588.
(5) Orwoll, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 6822.
(6) Rodriguez, A. T.; Patterson, D. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 501.
(7) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(8) (a) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 206. (b) *Ibid.* **1975**, *8*, 211.
(9) Kleintjens, L. A.; Koningsveld, R. *Colloid Polym. Sci.* **1980**, *258*, 711.
(10) Patterson, D.; Delmas, G.; Somcynsky, T. *Polymer* **1967**, *8*, 503.
(11) Hamada, F.; Fujisawa, K.; Nakajima, A. *Polym. J.* **1973**, *4*, 316.
(12) Somcynsky, T. *Polym. Eng. Sci.* **1982**, *22*, 64.
(13) Patterson, D.; Bardin, J. M. *Trans. Faraday Soc.* **1970**, *66*, 321.
(14) Jain, R. K.; Simha, R.; Balik, C. M. *Indian J. Pure Appl. Phys.*, in press.
(15) (a) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1491. (b) *Ibid.* **1980**, *18*, 897. (c) *Ibid.* **1982**, *20*, 1483.
(16) Jain, R. K.; Simha, R. *Polym. Eng. Sci.* **1979**, *19*, 845.
(17) Freeman, P. I.; Rowlinson, J. S. *Polymer* **1960**, *1*, 20.
(18) Nakajima, A.; Hamada, F. *Kolloid-Z.* **1965**, *205*, 55.