

Activity Coefficients in Nearly Athermal Model Polymer/Solvent Systems

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Constant pressure Monte Carlo simulations were performed to study the activity coefficients of bead-spring polymers dissolved in a monomeric solvent. Activity coefficients were obtained for binary mixtures of monomer and 20-mer for compositions ranging from pure 20-mer to pure solvent, using the chain increment method to obtain the chemical potentials of long-chain solute and monomeric solvent. Infinite dilution activity coefficients were also calculated for polymeric solutes in monomeric solvents and monomeric solutes in polymeric solvents solutions with chain length up to 60. Such detailed information on activity coefficients in polymer/solvent systems with large size differences had not been available previously from simulation or experiment. Several engineering models were tested for their ability to predict the activity coefficients in these nearly athermal systems. Results indicate that simple free-volume models can provide us with qualitatively accurate predictions for both short-chain solvent and long-chain solutes, provided that the functional form of the free-volume dependence is chosen appropriately.

Introduction

Phase equilibria play a crucial role in the design of polymer manufacturing processes. Knowledge of the phase behavior of polymer/solvent solutions is especially important for polymer production and purification operations. However, the predictive ability of engineering models describing such mixtures is still rather limited. There is therefore significant practical and theoretical interest in better understanding the thermodynamics of mixtures of large and small molecules.

A common method for estimating activity coefficients for process design is to use engineering correlations and theoretically based models. Models typically contain adjustable parameters that need to be obtained by fitting experimental data. Thus, if accurate predictions are desired, we need to have at least a few reliable data points. However, available experimental data, especially for long-chain solutes or polymers, are often of poor quality or not available altogether. For liquid mixtures of components with similar volatilities, the infinite dilution activity coefficients for all components can be obtained by differential ebulliometry (Nicolaidis and Eckert, 1978; Lobien and Prausnitz, 1982). For mixtures of

components that differ greatly in volatility, gas-liquid chromatography is often used to obtain the infinite dilution activity coefficients for the more volatile components (Parcher et al., 1975). However, several factors such as nonequilibrium effects and liquid or solid surface adsorption may cause complications. Moreover, this chromatographic method cannot be used to measure the infinite-dilution activity coefficient of the heavy component. Experimental data for activity coefficients of long-chain solutes in short-chain solvents have only been obtained from solid-liquid equilibrium measurements (Kniaz, 1991) for limited ranges of the chain length ratio. In these measurements, the thermal properties for the long-chain solute, such as the enthalpy change on melting and the phase transition from crystalline phase to mixture, must be known in order to estimate the activity coefficients. The resulting activity coefficient values are subject to significant measurement uncertainties.

Molecular simulations can provide an intermediate layer between direct experimental measurements and engineering models. They can offer unambiguous data for well-defined model systems to use for validation of approximate theoretical techniques. A number of recent developments have greatly

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expanded the range of the polymeric systems that can be practically studied by simulation with respect to their phase equilibrium behavior. For example, Siepmann (1990), Frenkel et al. (1992), and de Pablo et al. (1992) have proposed novel biased insertion methods to estimate chemical potentials of long-length chain systems. A related scheme was proposed by Harris and Rice (1988) to study intramolecular and intermolecular ordering in a supported monolayer of amphiphile molecules. These methods have the advantage that they can be used to obtain the chemical potential of full chains from a single simulation and are applicable to heteropolymers. However, the uncertainties in the chemical potential increase with chain length and density (Mooij, 1993). Direct calculations of phase coexistence of long-chain systems (Mooij et al., 1992; Laso et al., 1992) are possible by combining configurational-biased sampling with the Gibbs ensemble technique of Panagiotopoulos (1987). Siepmann et al. (1993) have obtained phase equilibria for alkanes up to C_{48} using this technique.

The recently proposed chain increment method (Kumar et al., 1991) can be used to obtain the incremental chemical potential between chains with lengths n and $n+1$. The total chemical potential of a chain can be obtained by sequentially summing the incremental chemical potentials of all chains of shorter length. It has been found (Szeleifer and Panagiotopoulos, 1992; Sheng et al., 1994) that the chain-length dependence of the incremental chemical potential is often weak and in practice only a few simulations are required to estimate the full chain chemical potentials. This method has been applied to obtain the phase diagram of chains with lengths up to 100 (Panagiotopoulos and Szeleifer, 1992; Sheng et al., 1994). While more cumbersome than configurational-bias methods, it is subject to less statistical noise for long chain lengths and high densities. The polymer/solvent mixtures studied here have high densities that are out of the range of applicability of the configurational-bias method since the probability of successfully inserting a whole chain into these dense systems is extremely low. It is much more probable for a single bead to be successfully inserted. Thus, we chose the chain increment method to be the simulation method used in the present work.

Group-contribution-based activity coefficient models (for example, the UNIFAC model of Fredenslund et al., 1977) are widely applied for chemical process modeling. However, the original UNIFAC model often results in large deviations from experimental data when applied to athermal or nearly athermal polymer/solvent systems. Empirical modifications of the UNIFAC model (Kikic et al., 1980; Larsen et al., 1987) have been proposed to overcome the tendency to overestimate the degree of nonideality, but many of the important features of polymer solution behavior still cannot be explained. For example, the existence of lower critical solution temperatures (LCST) suggests that in addition to the combinatorial term, there are other factors that play a role in polymer solution thermodynamics. As suggested by Patterson (1969, 1982), a possible such factor is free volume dissimilarity. Free volume is a somewhat loosely defined concept in polymer thermodynamics that has to do with the "voids" in a polymeric melt or glass that can accommodate small molecules or segments of larger molecules without much distortion of the structure of the polymer. Activity coefficient models that take into account both size and free volume ef-

fects (Elbro et al., 1990; Oishi and Prausnitz, 1978) do a better job in predicting solvent activity coefficients (Kontogeorgis et al., 1994). The ability of these free volume models to represent the activity coefficients of long-chain solutes remains unclear. The main goal of the present work is to provide a direct comparison of the predictions of engineering models with simulation data for the activity coefficients in polymer/solvent systems. Activity coefficients of both species in nearly athermal binary mixtures of short and long molecules are obtained for the first time from Monte Carlo simulations.

The plan of this article is as follows. Immediately after this introduction, we present the activity coefficient models studied. A section on model and methods outlines the constant-pressure Monte Carlo scheme we use to obtain activity coefficients of polymer/solvent solutions. The approximate chain increment method and efficient bond-weighted sampling of the incremental chemical potential are also discussed in this section. The section that follows contains results of the Monte Carlo simulations. Comparisons are made between Monte Carlo simulation data and the predictions by the activity coefficient models. We discuss features of the activity coefficient models that can best represent simulation results. We close by summarizing the main conclusions of this work.

Thermodynamic Background and Activity Coefficient Models

The well-known Flory-Huggins polymer solution theory (Flory, 1953) has been used extensively for studying the phase behavior of polymeric systems. For a binary mixture, the Gibbs free energy of mixing is expressed as

$$\frac{\Delta G^{\text{mix}}}{RT} = [\varphi_1 \ln \varphi_1 + \varphi_2 \ln \varphi_2] + \chi \varphi_1 \varphi_2. \quad (1)$$

The first two terms account for differences in size and shape of the molecules and are called the *combinatorial* part, while the last takes into account energetic contribution and is called the *residual* part.

According to the theory, for nearly athermal mixtures (for instance, hydrocarbon mixtures), any deviations from ideality in the liquid phase are essentially due to combinatorial effect, and from Eq. 1, one can obtain

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i}, \quad (2)$$

where φ_i is the segment fraction of component i :

$$\varphi_i = \frac{x_i r_i}{\sum_j x_j r_j}, \quad (3)$$

where x_i and r_i are mole fraction and van der Waals volume of component i , respectively.

The group contribution UNIFAC model (Fredenslund et al., 1977) uses the combinatorial term of the UNIQUAC model (Abrams and Prausnitz, 1975), which has a form similar to the Flory-Huggins expression except that the hard-core volumes were taken from the van der Waals volume as tabu-

lated by Bondi (1968), while the hard-core volumes in the original Flory–Huggins expression were calculated with Flory's equation of state from volumetric pure component properties. Several studies (Kikic et al., 1980; Larsen et al., 1987; Elbro et al., 1990; Kontogeorgis et al., 1994) showed that the Flory–Huggins/UNIFAC model tends to overestimate the degree of nonideality for alkane mixtures. A modified form for the activity coefficients has been proposed (Kikic et al., 1980; Larsen et al., 1987) to overcome this problem. The segment fraction in Eq. 3 has been empirically modified to be

$$\varphi_i = \frac{x_i r_i^p}{\sum_j x_j r_j^p} \quad (4)$$

Kikic et al. (1980) and Larsen et al. (1987) suggested that the exponent p be set equal to $2/3$. We denote this modified UNIFAC model by m-UNIFAC. This model shows improvements over the original UNIFAC model, but its predictions are still not satisfactory. Important features, such as lower critical solution temperature (LCST), cannot be explained. Patterson (1969, 1982) suggested that a possible factor for the existence of LCST is free-volume dissimilarity. The free-volume effect is usually coupled with the other effects, for example, the energetic interactions, and it exists even with no energetic effect. Many activity coefficient models have been proposed to take into account the free-volume contribution. For example, Oishi and Prausnitz (1978) used an explicit expression of $\ln \gamma_i$ based on equation-of-state theory proposed by Flory. However, it has the disadvantage that empirical parameters are needed. A new equation that combines combinatorial and free-volume contributions has been derived from a van der Waals free-volume expression by Elbro et al. (1990). Free volume is defined as the difference between the molar volume and the molar hard-core volume ($V_f = v - v^{hc}$). The molar hard-core volume is calculated from the van der Waals volumes given by Bondi (1968). The activity coefficients from this approach has the form of Eq. 2, with the volume fraction φ_i denoting the fraction of free volume associated with component i :

$$\varphi_i = \frac{x_i (v_i - v_i^{hc})}{\sum_j x_j (v_j - v_j^{hc})} \quad (5)$$

A modified form of the Elbro free-volume (Elbro-FV) model, which is called the p-FV model, incorporates a system-dependent exponent in the model. This model exponent depends on the van der Waals volumes of the two components:

$$\varphi_i = \frac{x_i (v_i - v_i^{hc})^p}{\sum_j x_j (v_j - v_j^{hc})^p}, \quad \dot{p} = 1 - \frac{v_{\text{small}}^{hc}}{v_{\text{large}}^{hc}} \quad (6)$$

where “small” and “large” denote the components of lowest and highest van der Waals volume, respectively. In Table 1, we summarize the activity coefficient models to be compared with Monte Carlo simulation results in this work.

Table 1. Summary of the Models Considered

Common for all Models: $\ln \gamma_i = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i}$, where φ_i is given by:			
UNIFAC	m-UNIFAC	Elbro-FV	p-FV
$\frac{x_i r_i}{\sum_j x_j r_j}$	$\frac{x_i r_i^p}{\sum_j x_j r_j^p}$	$\frac{x_i (v_i - v_i^{hc})}{\sum_j x_j (v_j - v_j^{hc})}$	$\frac{x_i (v_i - v_i^{hc})^p}{\sum_j x_j (v_j - v_j^{hc})^p}$
	$p = 2/3$		$p = 1 - v_{\text{small}}^{hc}/v_{\text{large}}^{hc}$

Model and Methods

Model

The polymer/solvent solutions studied in this work consisted of a collection of model chains each of length n immersed in their own monomeric beads. As in previous work (Sheng et al., 1994; Kumar et al., 1991), polymer chains were modeled as beads connected by stiff springs. The interactions between monomeric solvent beads and nonbonded beads were through the standard Lennard–Jones potentials.

$$U_{nb} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (7)$$

where ϵ and σ are the energy and size parameters, respectively. The monomeric ϵ and σ were used as reducing parameters to obtain all reduced quantities. The van der Waals or “hard-core” volumes required for use with the activity coefficient models of Table 1 were obtained by using $\pi\sigma^3/6$ for the monomer and $n\pi\sigma^3/6$ for the polymer. The potential was truncated at a distance of half the simulation box length and long-range corrections were added to all calculated thermodynamic quantities assuming that the segment–segment radial distribution function is unity for distances greater than half the box length (Allen and Tildesley, 1987). The interactions between bonded beads were represented by a harmonic spring potential as

$$U_b = \frac{1}{2} \kappa (r - \sigma)^2, \quad 0.5 < \frac{r}{\sigma} \leq 1.5. \quad (8)$$

The potential is infinite elsewhere. We have chosen $\kappa\sigma^2/\epsilon = 400$, consistent with previous studies (Sheng et al., 1994; Kumar et al., 1991).

The chain model we employ in this study involves significantly fewer constraints to the motion of internal beads than realistic models that include bond angle and/or torsional potential terms (Siepmann et al., 1993; de Pablo et al., 1992). Thus, loss of correlation between initial and final positions and conformations occurs over short distances along the chain. The flexibility of this chain model allows modeling of longer effective chain lengths with fewer beads than for realistic chain models.

In the present work we concentrate on solutions of chains in their own monomers. However, the simulation method is readily extendible to polymer/solvent systems for which the polymer may not be in solution of its own monomer. By adjusting the energy and size parameters of polymer–polymer,

polymer-solvent, and solvent-solvent interactions the thermodynamic properties of a wide selection of polymeric materials can be investigated.

Simulation details

The systems studied contained a total of 600 to 1,000 beads, depending on the length of the chains employed. Periodic boundary conditions were assumed in all three directions. The simulations were performed under conditions of constant temperature, pressure, and total number of particles. Pressure was set to near-atmospheric ($P^* = 0$) and the reduced temperature ($T^* = kT/\epsilon = 1.15$) was chosen so that the solvent is below its critical point, which is at $kT_c/\epsilon = 1.30$. The properties of interest (chemical potential and density) are less sensitive to system size than properties such as chain dimensions. We have performed a check run with doubled system size (2,000 beads) and find that the resulting chemical potential and density are in good agreement with the results of the smaller system size typically employed.

The initial configuration in all cases was a random one obtained by growing all the chains to the desired length in a way similar to the configurational-biased insertion method (Frenkel et al., 1992; de Pablo et al., 1992) and then randomly placing the monomeric solvent molecules into the system. The mixtures were equilibrated for 5–20 million Monte Carlo steps, depending on the compositions studied. For mixtures rich in long-chain molecules, the equilibration periods are longer than for monomer-rich solutions. The chemical potentials were then calculated based on the chain increment method (Kumar et al., 1991)—a modified version of the test particle insertion method of Widom (1963). However, the resulting densities ($\rho^* > 0.8$ for the polymer-rich solutions) of our systems are close to the limit of practical applicability of this method. Thus long production periods, 20–50 million Monte Carlo steps, were needed, and 50–100 million test bead insertions steps were performed in order to obtain reliable chemical potential estimations.

The moves employed for chains were reptation and bead displacement motions (Sheng et al., 1994). The solvent particles were moved via regular particle displacement moves. The new configurations resulting from these moves were accepted according to the standard Metropolis acceptance criterion (Allen and Tildesley, 1987). The constant-pressure condition was imposed for all the systems studied by allowing the volume of the simulation box to fluctuate. The coordinates of the chains and solvents were changed by scaling of the centers of mass for each molecule (chains and monomers) to the new volume. Details on the constant-pressure simulations are given in our previous work (Sheng et al., 1994).

The chain increment method

The calculation of the chemical potentials for the polymer chains was based on the chain increment method proposed by Kumar et al. (1991). As mentioned in our previous work (Sheng et al., 1994) the chain-length dependence of the chemical potential for bead-spring models is found to be weak. This contrasts with the behavior of the incremental chemical potential for a realistic chain model (de Pablo et al., 1992), which was observed to approach an asymptotic value only for significantly longer chains. A previous approximate

calculation of phase diagrams for the bead-spring model we are using has been performed by Panagiotopoulos and Szeleifer (1992). In that calculation, the chain-length dependence of the chemical potential was ignored, and the results compared well with the calculated phase diagram of Sheng et al. (1994). Based on this finding, a similar approach was introduced to overcome the difficulties involved in calculating the incremental chemical potentials of all chains of shorter length at these high-density conditions. The incremental chemical potential of the first bead shows the greatest deviation from the asymptotic value. Thus, instead of sequentially summing the incremental chemical potentials of all chains of shorter length, the chain chemical potential of length n , $\mu_r^{\text{chain}}(n)$, can be approximated as

$$\mu_r^{\text{chain}}(n) = \mu_r^+(1) + (n-1) \times \mu_r^+(n), \quad (9)$$

where $\mu_r^+(1)$ is the incremental chemical potential of the solvent as well as the first bead, and $\mu_r^+(n)$ is the asymptotic incremental chemical potential. By neglecting the chain-length dependence effect after the first bead, the approximated chain chemical potentials are slightly overestimated. However, we expect this approximation to have less effect on the activity coefficient calculations than on the phase equilibrium calculations, since calculations of activity coefficients involve subtraction between two overestimated chemical potentials and cancellation of error will result in answers close to the exact value.

Bond-weighted sampling

To further increase the efficiency of sampling, we incorporated Smit et al.'s (1992) suggestion in our calculations. The definition of incremental chemical potential, $\beta\mu_r^+$, is

$$\exp(-\beta\mu_r^+) = \frac{\int \int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 \exp[-\beta(U_b(r) + U_{nb}(X;r))] dr dX}{\int \int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 dr dX}. \quad (10)$$

It can be decomposed into two terms as follows,

$$\exp(-\beta\mu_r^+) = \frac{\int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 \exp(-\beta U_b(r)) dr \int dX \exp(-\beta U_{nb}(X;r))}{\int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 \exp(-\beta U_b(r)) dr \int dX} \times \frac{\int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 \exp(-\beta U_b(r)) dr}{\int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 dr}, \quad (11)$$

where the first term on the righthand side of Eq. 11 is denoted as “nonbonded” contribution, $\exp(-\beta\mu_{r,nb}^+)$, and the second term as “bonded” contribution, $\exp(-\beta\mu_{r,b}^+)$, to the incremental chemical potential. The nonbonded contribution, $\beta\mu_{r,nb}^+$, is calculated by choosing the distance l between

Table 2. Reduced Density, Excess Volume, Excess Enthalpy, Incremental Chemical Potentials for Monomer and Nonbonded Part of the Incremental Chemical Potential of the 20th-mer, and Activity Coefficients for Monomer and 20-mer at Different Segment Fractions for a Monomer/20-mer Binary Mixture at $T^* = 1.15$ and $P^* = 0^*$

φ_2	ρ^*	$V^{*,E}$	$H^{*,E}$	$\beta\mu_r^+ 1$	$\beta\mu_{r,nb}^+(n)$	$\ln \gamma_1$	$\ln \gamma_2$
0.0000	0.578(5)	0.000	0.000	-2.68(3)	-2.69(3)	0.00	-7.1(6)
0.0400	0.599(6)	-0.052	-0.056	-2.68(3)	-2.68(3)	-0.00(6)	-6.9(6)
0.1680	0.652(4)	-0.111	-0.188	-2.64(4)	-2.65(4)	-0.01(7)	-6.4(7)
0.3822	0.729(4)	-0.145	-0.277	-2.50(6)	-2.62(7)	-0.03(9)	-5.8(8)
0.5128	0.761(5)	-0.124	-0.297	-2.36(8)	-2.55(8)	-0.06(11)	-4.5(9)
0.8695	0.846(4)	-0.033	-0.090	-1.81(8)	-2.38(7)	-0.49(11)	-1.7(8)
0.9523	0.861(3)	-0.013	-0.031	-1.83(8)	-2.26(7)	-1.09(11)	-0.1(8)
1.0000	0.867(3)	0.000	0.000	-1.70(8)	-2.23(8)	-1.60(11)	0.00

*Statistical uncertainties are indicated in parentheses in the units of the last decimal point shown.

the test bead and the end of the chain with probability proportional to $r^2 \exp[-\beta U_b(r)]$ in the interval $0.5\sigma < r \leq 1.5\sigma$.

The bonded part is only a function of temperature and is independent of chain length. Thus, although the bonded part of the incremental chemical potential is usually 1 to 2 orders of magnitude larger than the nonbonded part, it is actually the "trivial" term. It can be obtained analytically at low to moderate temperatures because of the relatively sharp distribution of $\exp[-\beta U_b(r)]$ near $r = \sigma$. The numerator of the bonded contribution can be integrated to be

$$\int_{0.5\sigma}^{1.5\sigma} 4\pi r^2 \exp(-\beta U_b(r)) dr \equiv 4\pi^{3/2} \left[\frac{1}{2} \left(\frac{1}{\alpha^{3/2}} \right) + \left(\frac{1}{\alpha^{1/2}} \right) \right], \quad (12)$$

where $\alpha = 200\beta$ for our model. Trial insertions of the test beads with bond lengths deviating a lot from σ happen infrequently because l is sampled according to the probability of $r^2 \exp[-\beta U_b(r)]$. Large positive bond interaction energies resulting from bonds being compressed or stretched make no contribution to the ensemble average of the chemical potential. By employing this sampling scheme, we can save time by avoiding these unwanted trial insertions.

Activity coefficient calculation

The configurational chemical potential is

$$\beta\mu_{i,c}(x_2) = \beta\mu_{i,r}(x_2) + \ln \rho_N, \quad (13)$$

where x_2 is the composition of the polymer, and $\rho_N (= N/V)$ is the molecular density. The state of pure liquid i at the temperature and pressure of the solution is taken as standard state, thus

$$\ln \gamma_1(x_2) = \beta\mu_{1,c}(x_2) - \beta\mu_{1,c}(x_2 = 0) \quad (14)$$

$$\ln \gamma_2(x_2) = \beta\mu_{2,c}(x_2) - \beta\mu_{2,c}(x_2 = 1) \quad (15)$$

where γ_1 and γ_2 represent the activity coefficients of solvents and polymers. The infinite dilution activity coefficients were calculated as follows:

$$\ln \gamma_1^\infty = \beta\mu_{1,c}(\infty) - \beta\mu_{1,c}(\text{solvent}) \quad (16)$$

$$\ln \gamma_2^\infty = \beta\mu_{2,c}(\infty) - \beta\mu_{2,c}(n\text{-mer}), \quad (17)$$

where ∞ means the infinite dilution condition.

Results and Discussion

Details of the results for the monomer/20-mer mixtures as a function of composition are given in Table 2 and presented graphically in Figures 1 and 2. The excess volumes were calculated according to the following definition,

$$V^{*,E} = \frac{1}{\rho^*} - \left(\frac{\varphi_1}{\rho_1^*} + \frac{\varphi_2}{\rho_2^*} \right), \quad (18)$$

where φ_1 and φ_2 are the segment fractions of monomeric solvent and long-chain solute; ρ^* is the reduced segment density of the mixtures; and ρ_1^* and ρ_2^* represent the reduced segment densities of pure solvent and solute. The table indicates that the excess volumes of mixing are far from negligible and negative. If plotted against composition, the excess volume curve will be skewed as shown by Sánchez and Losada (1991). The reduced excess enthalpy of the mixture is defined as

$$H^{*,E} = H^* - (\varphi_1 H_1^* + \varphi_2 H_2^*), \quad (19)$$

where H^* is the reduced enthalpy (equal to the reduced en-

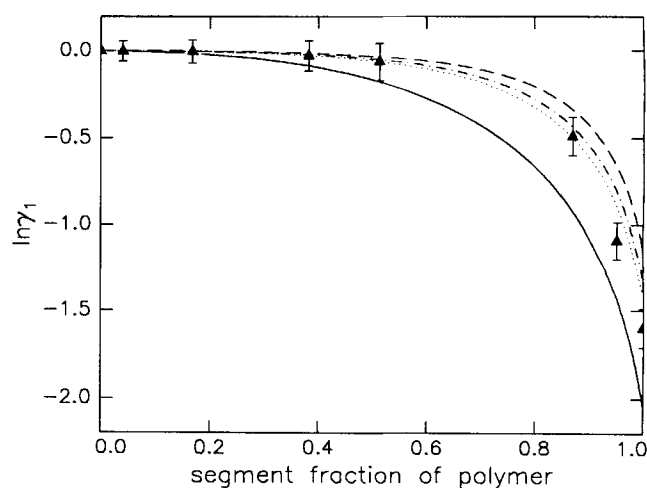


Figure 1. Calculated and predicted monomer activity coefficients, $\ln \gamma_1$ vs. segment fraction of polymer in a monomer/20-mer mixture.

(Δ) Represents MC results; (---) represents *m*-UNIFAC; (-·-·-) *p*-FV; (.....) Elbro-FV; (—) UNIFAC models, respectively.

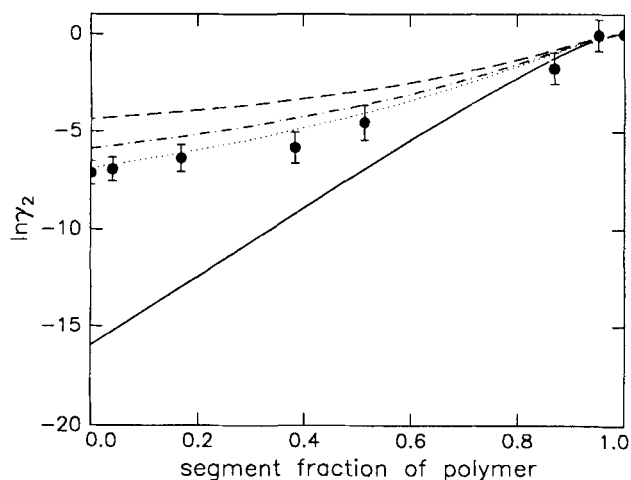


Figure 2. Calculated and predicted chain activity coefficients, $\ln \gamma_2$ vs. segment fraction of polymer in a monomer/20-mer mixture.

(●) Represents MC results; (---) represents *m*-UNIFAC; (-.-.-) *p*-FV; (.....) Elbro-FV; (—) UNIFAC models, respectively.

ergy, since $P^* = 0$) per segment. The maximum excess enthalpy shown in the table (for $\varphi_2 = 0.5128$) represents a 6.5% deviation from a completely athermal mixture. In the table, $\beta\mu_r^+(1)$ is the residual chemical potential of the monomeric bead as well as the incremental chemical potential of the first bead of polymer chains, which can be estimated by inserting test beads randomly into the fluid. Similarly, $\beta\mu_{r,nb}^+(n)$ represents the bond-weighted nonbonded part of the residual incremental chemical potential of the end bead. For $T^* = 1.15$, $\beta\mu_{r,b}^+ = 2.084$; however, as we mentioned in the previous section, the bonded part is actually only a trivial term in activity coefficient calculations.

We have also calculated activity coefficients of monomer mixing with higher straight-chain model polymers at infinite dilution, where the maximum degree of nonideality is expected. Information on the infinite dilution activity coefficients for long-chain molecules is difficult to obtain from experiments. The Monte Carlo results are tabulated in Table 3 and presented graphically in Figures 3 and 4, together with results from the four empirical models considered in this study.

The following comments summarize our observations on the comparison between the Monte Carlo results and the ac-

Table 3. Segment Densities, Incremental Chemical Potentials, and Infinite Dilution Activity Coefficients of Monomeric Beads and Model Chain for Different Chain Lengths at $T^* = 1.15$ and $P^* = 0^*$

<i>n</i>	ρ^*	$\beta\mu_r^+(1)$	$\beta\mu_{r,nb}^+(n)$	$\ln \gamma_1^\infty$	$\ln \gamma_2^\infty$
1	0.578(5)	-2.68(3)	-2.69(3)		
5	0.835(3)	-1.89(7)	-2.41(7)	-0.53(10)	-0.7(3)
10	0.857(3)	-1.79(8)	-2.25(8)	-1.01(11)	-3.5(5)
20	0.867(3)	-1.70(8)	-2.20(7)	-1.60(11)	-7.1(6)
30	0.869(4)	-1.68(7)	-2.19(8)	-1.98(10)	-12.5(7)
40	0.874(4)	-1.65(7)	-2.17(9)	-2.24(10)	-18.0(8)
50	0.877(5)	-1.63(13)	-2.15(9)	-2.44(16)	-24(1)
60	0.877(4)	-1.63(12)	-2.15(9)	-2.62(15)	-29(2)

*Statistical uncertainties are indicated in parentheses in the units of the last decimal point shown.

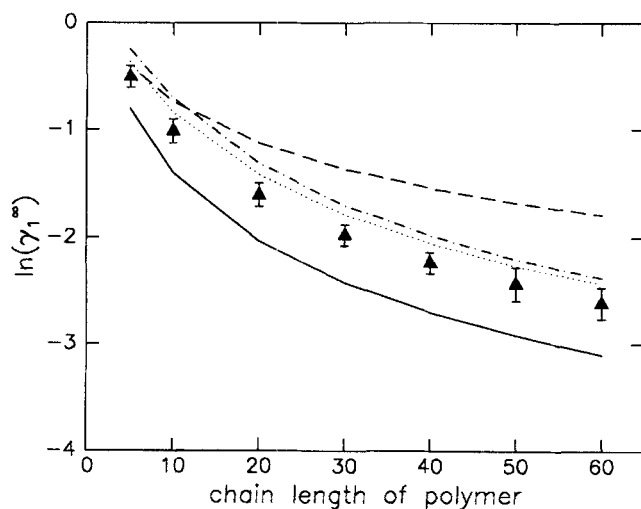


Figure 3. Calculated and predicted infinite dilution monomer activity coefficients, $\ln \gamma_1^\infty$ vs. chain length.

(▲) Represents MC results; (---) represents *m*-UNIFAC; (-.-.-) *p*-FV; (.....) Elbro-FV; (—) UNIFAC models, respectively.

tivity coefficient models. There are no adjustable parameters that enter in this comparison, so that agreement between models and simulation results is not forced in any way.

1. The original UNIFAC model underpredicts the infinite-dilution and finite-concentration γ values of the monomer in the chain fluids, which is in agreement with the observations of Oishi and Prausnitz (1978) and Kikic et al. (1980).

2. The modified UNIFAC model overpredicts the γ values of the monomer in the chain fluids. This appears to be in disagreement with the findings of Kontogeorgis et al. (1994) for solutions of small in large alkanes. However, the size ra-

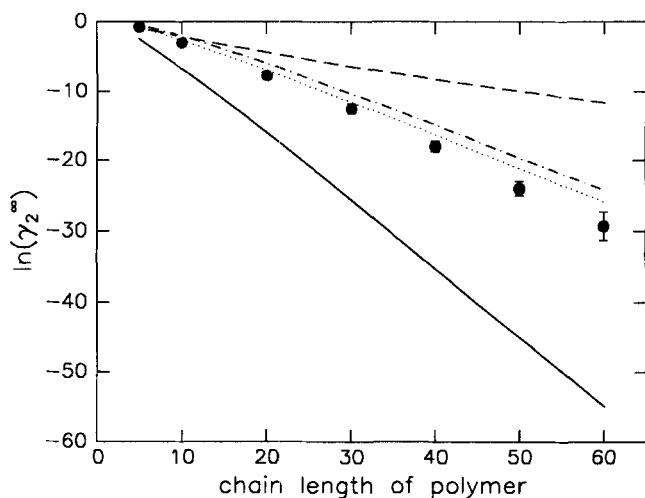


Figure 4. Calculated and predicted infinite dilution chain activity coefficients, $\ln \gamma_2^\infty$ vs. chain length.

(●) Represents MC results; (---) represents *m*-UNIFAC; (-.-.-) *p*-FV; (.....) Elbro-FV; (—) UNIFAC models, respectively.

tion in the study of Kontogeorgis et al. was less than 5, significantly below the ratios considered here. The findings from the present study, on the other hand, are in agreement with the Kontogeorgis et al. findings for systems such as alkanes in polymers that have large-size ratios.

3 The Elbro-FV and p-FV models are in good agreement with simulation data for the γ values of the monomer in the chain fluids. This is in agreement with the findings of Kontogeorgis et al. (1994).

4. Activity coefficients shown in Figures 2 and 4 are the first, as far as we know, to appear in the literature for the large-size ratios involved. They allow testing of empirical models for activity coefficients of large molecules in small ones for nearly athermal solutions. Although difficult to measure, such γ values are important—among other applications—for liquid-liquid equilibria of polymer/solvent systems.

5. The original and modified UNIFAC models again underestimate and overestimate, respectively, the γ values. The Elbro-FV and p-FV models are in better agreement, with the Elbro-FV coming the closest overall to the simulation data. Again, this conclusion, which we obtained for systems with large-size ratios, is in disagreement with the earlier study of Kontogeorgis et al. (1994), who found that the modified UNIFAC model was better for small-size ratios.

It has been suggested that the failure of the UNIFAC model to take into account the free-volume changes caused by mixing is the primary reason for its poor performance (Patterson, 1982; Elbro et al., 1990). Our results indicate that by incorporating free-volume concepts, both Elbro-FV and p-FV models provide better predictions than the UNIFAC model. It should be noted, however, that even though the p-FV model reduces to the Elbro-FV model as the size difference between the two components of the mixtures increases, they give very different results for mixtures with small-size differences.

The UNIFAC model underestimates the activity coefficients and thus exaggerates the effect of the combinatorial contribution, whereas the modified UNIFAC model overestimates the activity coefficients of both solvent and solute for mixtures of components with large-size difference. Our results indicate that the exponent p for a UNIFAC-type model should actually fall between $2/3$ and 1 . Weidlich and Gmehling (1987) suggested $p = 3/4$ based on comparisons with experimental data. Donohue and Prausnitz (1975) proposed an expression for exponent p based on a function of the surface area-to-volume ratio, which varies with the type of molecule. Analysis of our results indicates that even at constant temperature, the best fitted p for Monte Carlo results varied from 0.8 to 0.9 as the chain length of the polymer increases. Also, the UNIFAC-type models predict temperature-independent activity coefficients, which is only valid if the excess enthalpy of mixing is zero. This does not agree with the experimental findings. Several experimental studies (see Elbro et al., 1990; Parcher et al., 1975) have shown that the infinite-dilution activity coefficients of alkanes in hydrocarbon mixtures increase with temperature over a sufficiently broad temperature range. This, in fact, means that p should be both temperature and chain length dependent. We did not attempt to study temperature effects in the present work because of computing time constraints.

The free-volume models provide better overall predictions than other models for the infinite-dilution activity coefficient. This confirms the importance of free-volume effects on the phase behavior of polymer/solvent solutions. In our study, we found that the free-volume content of polymers ranges between 30% and 40% , which is consistent with the findings of Elbro et al. (1990). The solvent, however, has a free-volume percent (66%) higher than expected ($40\text{--}50\%$). The explanation for this is that the temperature studied is close to the critical point for the solvent. The temperature-dependent nature of the free-volume models makes this type of model superior to UNIFAC-type models when there is only one main group present in a mixture. As shown by Elbro et al. (1990), the free-volume models can give a qualitatively correct trend for the increase in activity coefficients as temperature increases.

Honnell and Hall (1989) have developed equations of state for hard-sphere n -mer fluids and monomer/ n -mer mixtures based on the idea of excluded volume effect. Their results point to promising ways to develop new theoretically based activity coefficient model. Extensions of their work to more generalized polymer chain models based on calculations similar to the ones reported in this work are currently in progress.

Summary and Conclusions

Constant-pressure Monte Carlo simulations were used to obtain information on activity coefficients in mixtures of large with small molecules for which reliable experimental data are difficult to obtain. Activity coefficients of monomer/20-mer solutions and infinite-dilution activity coefficients of monomers mixing with chains with varying length ($n = 5\text{--}60$) were calculated. We compare the MC results with several activity coefficient models and study the range of applicability of these models. The polymer/solvent systems studied were set up as model chains mixing with their own monomers. The incremental chemical potential method was used to calculate the chemical potentials of the components in the mixtures. A biased sampling scheme was also incorporated into our simulations to improve sampling efficiency.

In this work we confirm the importance of free-volume effects in analyzing the thermodynamics of polymer/solvent mixtures. Activity coefficient models that incorporate free-volume effects provide overall better predictions than other models. The Elbro free-volume model, which takes into account both combinatorial and free-volume contributions, was shown to give quantitatively good predictions for the activity coefficients of polymer/solvent solutions. The UNIFAC model does not include free-volume changes on mixing and exhibits significant deviations from the Monte Carlo results. The modified UNIFAC model with exponent $p = 2/3$ tends to overestimate activity coefficients for both solvent and solutes of polymer/solvent mixtures, while the exponent 1 of the original UNIFAC model underestimates both activity coefficients.

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Notation

- k = Boltzmann's constant
 N = number of chains
 p = exponent
 r = van der Waals volume, except in Eqs. 7–12, in which it denotes distance between Lennard–Jones interaction centers
 U = energy
 X = relative positions of the nonbonded beads with respect to the test beads
 α = integration constant (Eq. 12)
 $\beta = 1/kT$
 χ = interaction parameter
 κ = harmonic spring constant in Eq. 8

Superscripts and subscripts

- comb = combinatorial term
 E = excess property
 mix = mixing properties
 res = residual term
 b = bonded contribution
 c = configurational property as in Eqs. 13–17, except in T_c , in which it denotes critical property
 r = residual part

Literature Cited

- Abrams, D. S., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).
 Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford Univ. Press, New York (1987).
 Bondi, A., *Physical Properties of Molecular Crystals, Liquids, and Glasses*, Wiley, New York (1968).
 de Pablo, J. J., M. Laso, and U. W. Suter, "Estimation of the Chemical Potential of Chain Molecules by Simulation," *J. Chem. Phys.*, **96**, 6157 (1992).
 Donohue, M. D., and J. M. Prausnitz, "Combinatorial Entropy of Mixing Molecules that Differ in Size and Shape. A Simple Approximation for Binary and Multicomponent Mixtures," *Can. J. Chem.*, **53**, 1586 (1975).
 Elbro, H. S., Aa. Fredenslund, and P. Rasmussen, "A New Simple Equation for the Prediction of Solvent Activities in Polymer Solutions," *Macromolecules*, **23**, 4707 (1990).
 Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY (1953).
 Fredenslund, Aa., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria using UNIFAC*, Elsevier, New York (1977).
 Frenkel, D., G. C. A. M. Mooij, and B. Smit, "Novel Scheme to Study Structural and Thermal Properties of Continuously Deformable Molecules," *J. Phys. Condens. Matter*, **4**, 3053 (1992).
 Harris, J., and S. A. Rice, "A Lattice Model of a Supported Monolayer of Amphiphile Molecules: Monte Carlo Simulation," *J. Chem. Phys.*, **88**, 1298 (1988).
 Honnell, K. G., and C. K. Hall, "A New Equation of State for Athermal Chains," *J. Chem. Phys.*, **90**, 1841 (1989).
 Kikic, I., P. Alessi, P. Rasmussen, and Aa. Fredenslund, "On the Combinatorial Part of the UNIFAC and UNIQUAC Models," *Can. J. Chem. Eng.*, **58**, 253 (1980).
 Kniaz, K., "Solubility of *n*-Docosane in *n*-Hexane and Cyclohexane," *J. Chem. Eng. Data*, **36**, 471 (1991).
 Kontogeorgis, G. M., P. Coutisikos, D. P. Tassios, and Aa. Fredenslund, "Improved Models for the Prediction of Activity Coefficients in Nearly Athermal Mixtures: Part I: Empirical Modifications of Free-Volume Models," *Fluid Phase Equil.*, **92**, 35 (1994).
 Kumar, S. K., I. Szleifer, and A. Z. Panagiotopoulos, "Determination of the Chemical Potentials of Polymeric Systems from Monte Carlo Simulations," *Phys. Rev. Lett.*, **66**, 2935 (1991).
 Larsen, B. L., P. Rasmussen, and Aa. Fredenslund, "A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing," *Ind. Eng. Chem. Res.*, **26**, 2274 (1987).
 Laso, M., J. J. de Pablo, and U. W. Suter, "Simulation of Phase Equilibria for Chain Molecules," *J. Chem. Phys.*, **97**, 2817 (1992).
 Lobien, G. M., and J. M. Prausnitz, "Infinite-Dilution Activity Coefficients from Differential Ebulliometry," *Ind. Eng. Chem. Fundam.*, **21**, 109 (1982).
 Mooij, G. C. A. M., "Novel Simulation Techniques for the Study of Polymer Phase Equilibria," PhD Thesis, Univ. of Utrecht, The Netherlands (1993).
 Mooij, G. C. A. M., D. Frenkel, and B. Smit, "Direct Simulation of Phase Equilibria of Chain Molecules," *J. Phys. Condens. Matter*, **4**, L255 (1992).
 Nicolaidis, G. L., and C. A. Eckert, "Optimal Representation of Binary Liquid Mixture Nonidealities," *Ind. Eng. Chem. Fundam.*, **17**, 331 (1978).
 Oishi, T., and J. M. Prausnitz, "Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method," *Ind. Eng. Chem. Process Des. Dev.*, **17**, 333 (1978).
 Panagiotopoulos, A. Z., "Direct Determination of Phase Coexistence Properties of Fluids by Monte Carlo Simulation in a New Ensemble," *Mol. Phys.*, **61**, 813 (1987).
 Panagiotopoulos, A. Z., and I. Szleifer, "Monte Carlo Simulation of Phase Equilibria of Polymeric Fluids," *Poly. Prep. (Amer. Chem. Soc., Div. Poly. Chem.)*, **33**, 547 (1992).
 Parcher, J. F., P. H. Weiner, C. L. Hussey, and T. N. Westlake, "Specific Retention Volumes and Limiting Activity Coefficients of C₄–C₈ Alkane Solutes in C₂₂–C₃₆ *n*-Alkane Solvents," *J. Chem. Eng. Data*, **20**, 145 (1975).
 Patterson, D., "Free Volume and Polymer Solubility. A Qualitative View," *Macromolecules*, **2**, 672 (1969).
 Patterson, D., "Polymer Compatibility With and Without a Solvent," *Poly. Eng. Sci.*, **22**, 64 (1982).
 Sánchez, M. G., and C. R. Losada, "Excess Volumes of *n*-Hexane + *n*-Undecane between 288.15 and 308.15 K," *J. Chem. Eng. Data*, **36**, 75 (1991).
 Sheng, Y.-J., A. Z. Panagiotopoulos, S. K. Kumar, and I. Szleifer, "Monte Carlo Calculation of Phase Equilibria for a Bead-Spring Polymeric Model," *Macromol.*, **27**, 400 (1994).
 Siepmann, J. I., "Configurational-bias Monte Carlo: A New Sampling Scheme for Flexible Chains," *Mol. Phys.*, **70**, 1145 (1990).
 Siepmann, J. I., S. Karaborni, and B. Smit, "Simulations of Complex Fluids: Critical Properties of *n*-Alkanes," *Nature*, **365**, 330 (1993).
 Smit, B., G. C. A. M. Mooij, and D. Frenkel, "Comment on 'Determination of the Chemical Potential of Polymeric Systems from Monte Carlo Simulations'," *Phys. Rev. Lett.*, **68**, 3657 (1992).
 Szleifer, I., and A. Z. Panagiotopoulos, "Chain Length and Density Dependence of the Chemical Potential of Lattice Polymers," *J. Chem. Phys.*, **97**, 6666 (1992).
 Weidlich, U., and J. Gmehling, "A Modified UNIFAC Model: 1. Prediction of VLE, h^E , and γ^∞ ," *Ind. Eng. Chem. Res.*, **26**, 1372 (1987).
 Widom, B., "Some Topics in the Theory of Fluids," *J. Chem. Phys.*, **39**, 2808 (1963).

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