The Surface Tension of Polymer Blends: Theory and Experiment

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ABSTRACT: The surface tensions of a series of miscible polymer blends were measured using a modified Wilhelmy method. The results were compared with the Cahn-Hilliard theory where the Flory, Orwoll, and Vrij equation of state was used to model the bulk properties of the blends. Experimental results for blends of low and high molecular weight (MW) poly(dimethylsiloxane) (PDMS) were found to agree with theory to within experimental error with no adjustable parameters. The results indicate that we can accurately model the surface excess of the low molecular weight PDMS component. The theoretical dependence of the surface tension of the blend on the square gradient coefficient κ_{12} is also described. Blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) were also studied. Both theory and experiment indicated that there is a strong surface excess of PVME. The PS-PVME system is known to have an attractive specific interaction which gives rise to miscibility. This attractive potential was included in the theory via an interaction parameter, to give quantitative agreement between theory and experiment. The magnitude of the interaction term is consistent with that used for modeling the phase behavior of this system.

Introduction

The modification of the surface tension (γ) of polymer mixtures or blends is important in many fundamental areas such as compatibilization, wetting, foaming, and lubrication. To understand the basis for these and related phenomena, it would be useful to develop predictive tools which could be used to predict the surface properties including interfacial profiles and surface excesses. In a previous paper[1] we found that the Cahn-Hilliard (CH) theory[2] in conjunction with the Flory, Orwoll, and Vrij (FOV) equation of state[3] provided a unified description of the surface tensions of both oligomeric and polymer single-component liquids. In this work we extend the same theory to study the surface tension of polymer blends.

Theories of the surface tension of mixtures include the theory of Prigogine and Marechal[4] extended by Defay, Prigogine, et al.[5] and Gaines.[6] The theory assumes that the system is homogeneous up to a surface layer. The surface layer is assumed to be homogeneous but of different composition to the bulk. The free energy of the system has contributions from the bulk and the surface. The form of these contributions is determined by the microscopic model used to describe the system. The entropy of the system is described by the Flory-Huggins[7] expression, and hence the effect of the size of the molecules is taken into account. Interactions are taken into account in a manner similar to the Flory-Huggins model. One then equates the chemical potentials of the bulk and surface layers to obtain an expression for γ. A special case of this approach was used by Gaines.[6] The application of the Gaines theory to a mixture at a fixed temperature requires knowledge of the surface tensions of the pure components, their molar volumes, and an interaction parameter. The interaction parameter is assumed to be independent of the molecular weight. The theory provides a precise description of the dependence of the surface tension on composition for polymer-solvent and solvent-solvent mixture data.[6] In terms of oligomer blends, good agreement with experiment has been found[8] although reports of the corresponding experiments for mixtures of like polymers of different molecular weights are lacking.

For a pure liquid there is only one free energy and length scale of importance for the description of its physical properties. It was van der Waals[9] who first incorporated these ideas into a theory of the vapor-liquid surface. The CH theory extended the work of van der Waals. The CH theory allows one to calculate the surface tension and surface density profile using bulk thermodynamic properties. The bulk thermodynamic properties are obtained by fitting an equation of state to pressure, volume, and temperature (*PVT*) data for a sample. The equations of state used are those which enable us to compute entropies and enthalpies of the system using *PVT* data. In the application of the CH theory to single-component polymer systems, we found previously that the FOV equation provided a better description of the molecular weight and temperature dependence of γ for polymer liquids[1] when compared with the Sanchez-Lacombe[11] (SL) equation of state. It was also found that great care must be taken to ensure that the reduction parameters, which characterize the fit to the *PVT* data, provide an accurate description of the *PVT* data. Methods to overcome the inherent imprecision of the equations of state were described[1] which involve subdividing the *PVT* data into smaller pressure-temperature blocks for fitting. In this fashion we ensure that the density and other thermodynamic properties of the components to the mixture are well described by the reduction parameters obtained from the fitting procedure.

If the equation of state is derived from a partition function based on a microscopic model of the system, then it is easily extended to describe the thermodynamic properties of multicomponent mixtures. Poser and Sanchez[10] used the Sanchez-Lacombe[11] equation of state in their study of the surface and interfacial tensions of polymer and oligomer solutions. No polymer blends were studied in that work.[10] They found that they could predict the surface tension of mixtures for solvent-solvent and polymer-solvent systems with agreement comparable to that achieved by Gaines.[6] However, like Gaines, they used the square gradient coefficients to ensure that the surface tensions of the pure components were correct, and they also used an adjustable bulk interaction parameter to achieve quantitative agreement with experimental data. The use of these extra fitting parameters leads to some question as to the predictive power of such theories.

The results presented below indicate that in the cases where the random mixing approximation is expected to be valid, such as for PDMS/PDMS blends of different MW, the theory can be applied successfully with no adjustable parameters. In other cases of blends of

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dissimilar polymers, the specific interactions which drive bulk miscibility must be logically accounted for by invoking an interaction parameter in the equation of state theory.

Theory

The extension of the Cahn-Hilliard theory to multicomponent systems is well documented.[10] The application of the FOV equation of state to multicomponent systems has been described in great detail elsewhere,[12] and a calculation of the Gibbs free energy for a mixture is presented in Appendix 1. The use of the FOV equation in conjunction with the CH theory to describe the surface properties of mixtures has not been illustrated elsewhere. Poser and Sanchez[10] used the SL equation of state with the CH theory to study the surface and interfacial tension of polymer and oligomer solutions. In a previous comparison of the SL and FOV equations of state for single-component systems we found that the FOV model better described the experimental data for polymer liquid surface tensions. We will not compare the two theories here but refer the interested reader to the work of Poser and Sanchez.

The interfacial tension, γ, for a planar interface is of the form

$$\gamma = (A - A_e)/S_0 \tag{1}$$

where A is the Helmholtz free energy of the inhomogeneous system with the interface and A_e is the Helmholtz free energy of the system without the interface but with the same density and composition as the inhomogeneous system. S_0 is the surface area of the interface. To evaluate eq 1 we must compute expressions for A and A_e. The equation of state provides expressions for the enthalpy and entropy of a homogeneous mixture at a given density. Using these expressions we can compute A_e. To compute the free energy A, we need expressions for the entropic and enthalpic contributions from a system where an interface separates two different phases. These contributions will be of two types. The first are those which are functions of the local density. These can again be computed using the equation of state. The second are those which arise from the presence of gradients in composition. The form of the contributions to the enthalpy from the presence of gradients in composition can be computed from statistical mechanics. To leading order they give rise to the square gradient term whose coefficient is the second moment of the interaction potential in the mean field approximation. The entropic contributions from the presence of gradients are usually neglected. They can and have been calculated within the context of lattice models for liquid–vapor[13] interfaces. For liquid–vapor interfaces the entropic contributions from gradients are negligibly small compared with those due to the density variations. In the cases where there is a nonnegligible density change at a liquid–liquid interface we may also expect the dominant contribution to the entropy to be gradient independent.

For a two-component system the total Helmholtz free energy, A, can be written in the form

$$A = S_0\int \mathrm{d}x\, [a_0(x) + {}^1/_2\{\kappa_{11}(\partial\rho_1/\partial x)^2 + \kappa_{12}(\partial\rho_1/\partial x)(\partial\rho_2/\partial x) + \kappa_{22}(\partial\rho_2/\partial x)^2\}] \tag{2}$$

where $a_0(x)$ is the local Helmholtz free energy density, ρ_i are the number density of the mers of the respective components to the system, and the κ_{ij} are the coefficients of the square gradient terms which quantify the enthalpic contributions to the free energy from the presence of density gradients in the system.

Bongiorno, Scriven, and Davis[14] discuss the approximations inherent in the Cahn–Hilliard theory and relate it to other microscopic statistical mechanical models of liquid–vapor interfaces. In particular, they show that κ_{ij} is related to the local short-range order in the homogeneous phase by the following relationship:

$$\kappa_{ij}(\rho) = (kT/12)\int r^2 c^\circ{}_{ij}(r,\rho)\, \mathrm{d}^3r \tag{3}$$

where $c^\circ{}_{ij}(r,\rho)$ is the Ornstein–Zernike direct correlation function[15] at a density ρ in the homogeneous state. This expression for κ_{ij} is also obtained as an expansion in the density of the correlation function keeping the lowest order term.

The function $a_0(x)$ in eq 2 is computed based on the following microscopic model. A detailed discussion of the assumptions underlying the model can be found elsewhere.[12] For a single-component polymer liquid, each molecule is subdivided into r mers. The mers are placed in cells with one mer per cell. The mers are allowed to move within their cells and interact with each other via a pair potential which depends on the distance between the mers. The mers are assumed to have $3c$ degrees of freedom, where c is a constant less than one, reflecting the polymer character of the molecule. Each mer has a hard core volume v^*. The characteristic mer–mer interaction energy is ϵ^*. From these rather simplistic assumptions a partition function can be constructed and the following equation of state is obtained in the case where a van der Waals potential is used to model the interaction between the mers.

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{T}\tilde{v} \tag{4}$$

where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{v} = v_{\rm sp}/v_{\rm sp}{}^*$ are the reduced pressure, temperature, and specific volume, respectively. The reduction parameters are related to the microscopic parameters via the following relations. $P^* = \epsilon^*/v^*$, $T^* = \epsilon^*/ck$, and $v_{\rm sp}{}^* = Nrv^*/M$, where $v_{\rm sp}{}^*$ is the hard core specific volume, M is the molecular weight of the molecule, and k is the Boltzmann constant. The reduction parameters can be obtained by fitting eq 4 to PVT data.

The model is easily extended to model polymer mixtures.[12] The partition function for the mixed system is computed based on the assumption that the mers from the different components mix randomly. The hard core volumes of the mers are assumed to be equal. The mers have microscopic properties described by the parameters $\epsilon_i{}^*$, c_i, and r_i and corresponding macroscopic reduction parameters $P_i{}^*$, $T_i{}^*$, and $v_i{}^*{}_{\rm sp}$ which describe the thermodynamic properties of the components to the mixture. The calculation of the Gibbs free energy of mixing is presented in the appendix.

Writing A_e in the form

$$A_e = V(\rho_1\mu_1{}^e + \rho_2\mu_2{}^e) - P_eV \tag{5}$$

where $\mu_i{}^e$ is the equilibrium chemical potential of the ith component of the homogeneous mixture at a pressure P_e and V is the system volume. Using eqs 2 and 5 in eq 1, we obtain the following expression for the interfacial tension:

$$\gamma = \int \mathrm{d}x\, [\Delta a(x) + {}^1/_2\{\kappa_{11}(\partial\rho_1/\partial x)^2 + \kappa_{12}(\partial\rho_1/\partial x)(\partial\rho_2/\partial x) + \kappa_{22}(\partial\rho_2/\partial x)^2\}] \tag{6}$$

where

$$\Delta a(x) = a_0(x) - (\rho_1\mu_1^{\mathrm{e}} + \rho_2\mu_2^{\mathrm{e}}) + P_{\mathrm{e}} \tag{7}$$

Demanding that the solutions $[\rho_1(x), \rho_2(x)]$ minimize the surface excess energy in eq 6 yields the Euler–Lagrange equations, which for this two-component system are of the form

$$\kappa_{11}(\partial^2\rho_1/\partial x^2) + \kappa_{12}(\partial^2\rho_2/\partial x^2) - \partial\Delta a/\partial\rho_1 = 0 \tag{8a}$$

$$\kappa_{12}(\partial^2\rho_1/\partial x^2) + \kappa_{22}(\partial^2\rho_2/\partial x^2) - \partial\Delta a/\partial\rho_2 = 0 \tag{8b}$$

Using eqs 8 one can easily derive the following simplified expression for the interfacial tension:

$$\gamma = \int \mathrm{d}x\, \{\kappa_{11}(\partial\rho_1/\partial x)^2 + \kappa_{12}(\partial\rho_1/\partial x)(\partial\rho_2/\partial x) + \kappa_{22}(\partial\rho_2/\partial x)^2\} \tag{9}$$

and

$$\gamma = 2\int \mathrm{d}x\, \Delta a(x) \tag{10}$$

The square gradient coefficient, κ_{12}, can be computed within the context of a mean field approximation[10] where one assumes that the components to the mixture mix randomly. Under these circumstances we have that

$$\kappa_{12} = (\kappa_{11}\kappa_{22})^{1/2} \tag{11}$$

We solve eqs 8 for solutions using a relaxation method and use these solutions to compute the interfacial tension using eq 9 or 10.

Scaling

It is useful to write eqs 8 in reduced variables or in a scaled form. In the reduced form the equations are invariant for different systems and the properties of each system are determined by a few dimensionless parameters which are functions of the physical properties of the components of the mixture. Since we have two components we will choose the relevant scaling parameters from component 1. We can then define the following scaled variables:

$$\tilde{\gamma} = \gamma/\gamma^* \quad \text{and} \quad \Delta\tilde{a} = \Delta a/P^*_1$$

with $\gamma^* = \epsilon^*_1/v^*_1{}^{2/2}$, $\tilde{\kappa} = \kappa/\kappa^*$ with $\kappa^* = \epsilon^*_1 v^*_1{}^{5/3}$, $P^*_1 = \epsilon^*_1/v^*_1$, and $v^* = v^*_1 = v^*_2$. The form of $\Delta a(x)$ used depends on the equation of state used to model the bulk properties of the mixture. For the FOV model it takes the following form:

$$\Delta a = (\epsilon^*/v^*)\tilde{\rho}\{\tilde{P}\tilde{v} - 1/\tilde{v} - \tilde{T}(\ln v^* + 3\ln(\tilde{v}^{1/3} - 1)) + kT/\epsilon^*[\phi_1/r_1 \ln \phi_1 + \phi_2/r_2 \ln \phi_2]\} - \tilde{\rho}/v^*\{\phi_1\mu^{\mathrm{e}}{}_1 + \phi_2\mu^{\mathrm{e}}{}_2\} \tag{12}$$

where the chemical potentials $\mu^{\mathrm{e}}{}_i$ and the quantities ϕ_i (site fractions) are defined in the appendix. $\tilde{\rho} = 1/\tilde{v}$ and the number density of mers ρ_i is related to $\tilde{\rho}$ by the relation $\rho_i = \phi_i\tilde{\rho}/v^*$.

With these definitions eqs 8 can be written in the following form:

$$2\tilde{\kappa}_{11}(\partial^2\tilde{\rho}_1/\partial\tilde{x}^2) + 2\alpha^{1/2}\tilde{\kappa}_{12}(\partial^2\tilde{\rho}_2/\partial\tilde{x}^2) - \partial\Delta\tilde{a}/\partial\tilde{\rho}_1 = 0 \tag{13a}$$

$$2\alpha^{1/2}\tilde{\kappa}_{12}(\partial^2\tilde{\rho}_1/\partial\tilde{x}^2) + 2\alpha\tilde{\kappa}_{22}(\partial^2\tilde{\rho}_2/\partial\tilde{x}^2) - \partial\Delta\tilde{a}/\partial\tilde{\rho}_2 = 0 \tag{13b}$$

where $\alpha = P^*_2/P^*_1$ and $x = \tilde{x}v^{*1/3}$.

To calculate the surface tension from the scaled surface tension, we must write the microscopic reduction parameters in terms of the macroscopic reduction parameters as follows:

$$\gamma = \tilde{\gamma}P^*_1{}^{2/3}T^*_1{}^{1/3}(kc_1)^{1/3} \tag{14}$$

where $v^* = kc_1T^*_1/P^*_1$. The surface tension and the length scale of the problem, x, depend on the microscopic parameter c_1. In previous work the value of c_i was chosen so that the value of v^* reflected the volume of a polymer segment. In that case the value of the hard core volume varied as P^* and T^* varied with temperature and molecular weight. In the present case we fix the value of v^* and the value of c varies. The observation that $\tilde{\kappa}$ = constant for polymer and oligomer liquids[1] can be restated as $c_i{}^{1/3}\tilde{\kappa}_{ii}{}^{1/2}$ = constant for mixtures where we have demanded that $v^*_1 = v^*_2 = v^*$. In the calculations below the values of $\tilde{\kappa}_{ii}$ quoted are those obtained from previous work.[1] The value of $\tilde{\kappa}_{22}$ used in the calculations is modified so that the relation $c_1{}^{1/3}\tilde{\kappa}_{11}{}^{1/2} = c_2{}^{1/3}\tilde{\kappa}_{22}{}^{1/2}$ is obeyed.

Experimental Section

Materials. The PDMS samples were obtained from Scientific Polymer Products and have M_n = 32 000, 2600, and 770 with M_w/M_n = 2.22, 1.5, and 1.13, respectively. The PVME was obtained from Scientific Polymer Products and had M_n = 49 000 with M_w/M_n = 2. The PS was obtained from Polysciences and had M_n = 1850 with M_w/M_n = 1.195. Part of the PVME was purified by precipitating from warm water. Gel permeation chromatography showed that the low molecular weight tail was removed by this procedure but there was no change in the melt surface tension of this material compared to the unpurified sample. Thus, the as-received sample was used for all blend studies reported here.

The PDMS samples were melt blended with stirring and then allowed to equilibrate. The PVME blends were also melt blended with stirring by hand at temperatures above the T_g of PS. For the lower volume fractions of PVME (0.01, 0.1, and 0.6% PVME) both solvent blending (toluene) and melt blending were used with no apparent differences. For these samples which had glass transitions close to those of pure PS, the samples were annealed for 24 h at 110 °C to obtain an equilibrium surface composition.

Methods. The surface tensions were measured using the micro-Wilhelmy technique as was described previously.[16] No densities are needed for the determination of γ. The experiments were relatively fast because of rapid viscous relaxation of the polymer meniscus on the small-diameter bare glass fiber which was used as the Wilhelmy probe. Freshly prepared bare glass fibers were used to facilitate zero contact angle. At low temperatures for 100% PS and the high volume fraction PS blends with PVME, we have some evidence based on contact angle hysteresis in the melt that the system deviates slightly from zero contact angle. The data are still quite accurate in these regions compared to other techniques. The data were not corrected at these low temperatures due to the lack of an appropriate correction scheme. For all other data reported, no evidence of finite contact angles was observed.

The pressure–volume–temperature (*PVT*) data for the liquids were taken using the apparatus which has been described previously.[17] Before loading the *PVT* cell, densities of the liquids were measured using a specific gravity bottle. For the solid polymers at room temperature the densities were measured using an autopycnometer (Micrometrics).

Results

PVT data for each pure component used in the blends were obtained. The *PVT* data for the components were partitioned into small pressure–temperature domains. A reduced range of pressures and temperatures was chosen to ensure that the fit of the equation of state to the *PVT* data was within the experimental precision of the data. In this fashion the temperature-dependent reduction pa-

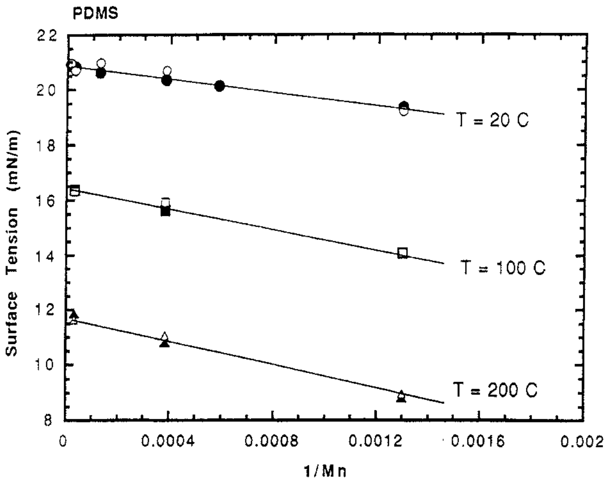

Figure 1. Plot of the surface tension of PDMS as a function of $1/M_n$ at T = 20, 100, and 200 °C.

rameters were obtained for each component. For further details of the fitting procedure, the interested reader is referred to ref 1. At the temperature of interest we used the reduction parameters for the two components to compute $\Delta a(x)$ using eq 12. We then solve eqs 13 for $\rho_1(x)$ and $\rho_2(x)$ using a relaxation technique.

PDMS Blends. As a first test of the theory we will study a blend composed of the same chemical species but with differing molecular weights. Changes in density on the order of 20% can occur in polymer liquids with changes in the degree of polymerization (DP) in the range 10 < DP < 1000. Changes in the density on this order can cause 100% change in the surface tension at high temperatures. Since many polymer samples exist as polydisperse mixtures, it is to be expected that in many cases these samples will have molecular weight distributions which have low molecular weight tails in the range 10 < DP < 1000. Under these circumstances the surface tension of such a sample will be affected by the low molecular weight component. Another reason to study a blend with the same chemical species but differing molecular weights is that it represents the simplest test of the efficacy of the thermodynamic mixing rules of the theory. We assume random mixing and that the interactions are of the simple dispersive kind. If the model fails to describe the properties of such a mixture, then its usefulness as a tool for predicting the properties of blends with dissimilar chemical structure is suspect.

To develop a better understanding of the system we wish to study, we will first illustrate the properties of different molecular weight monodisperse samples of PDMS. Figure 1 shows the molecular weight and temperature dependence of the surface tension for a number of PDMS samples. The open symbols denote the experimental measurements, and the solid symbols are the theoretical predictions for the pure component systems determined using *PVT* data for the different molecular weight samples. The value of $\tilde{\kappa}$ used was chosen so that the experimental and theoretical values agreed at 50 °C for the sample with molecular weight M_n = 770. The first advantage of the present model is that a single value of $\tilde{\kappa}$ can describe both the molecular weight and temperature dependence of the surface tension for the pure components. As we have demonstrated previously,[18] the surface tension shows a clear $1/M_n$ dependence at high molecular weights. The scatter is the theoretical data points is caused by errors which result from the measurement of the *PVT* properties. Errors in the determination of the density, for example, will result in errors in the calculation of the surface tension. In considering the properties of the blends, these errors will manifest themselves as shifts in the position of the pure component surface tension values. We should also note from Figure 1 that at any given temperature the range over which the surface tension varies is only on the order of 1–3 mN/m.

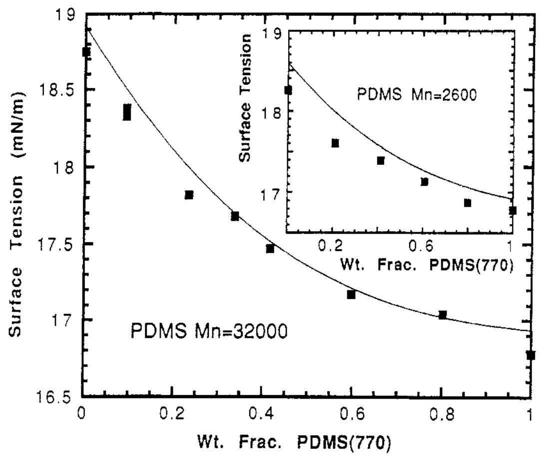

Figure 2. Surface tension of a blend of PDMS(M_n = 32 000) and PDMS(M_n = 770) as a function of the weight fraction of the low molecular weight component. The inset shows a similar plot with the higher molecular weight component replaced by a M_n = 2600 sample.

Since the PDMS samples are of the same chemical composition, the polymers interact with each other via simple dispersive interactions. On this basis we expect them to mix randomly. Thus the geometric mean approximation for both the bulk interaction parameter X_{12} and the square gradient coefficient $\tilde{\kappa}_{12}$ should be valid. The interaction parameter X_{12} defined in the appendix has the form

$$X_{12} = P^*_1 + P^*_2 - 2d_{12}(P^*_1P^*_2)^{1/2} \qquad (15)$$

and κ_{12} is defined by eq 11. The parameter d_{12} is set equal to 1 for the case of random mixing. Using nonunity values of d_{12} allows us to mimic interactions which are either more favorable ($d_{12} > 1$) or less favorable ($d_{12} < 1$) than that predicted by the random mixing approximation.

Figure 2 shows the experimental (filled symbols) and theoretical prediction (solid line) for the surface tension of the blend at T = 50 °C. The difference in surface tensions of the two components is very small, on the order of 2 mN/m. To our knowledge, these data for blends of different molecular weight polymers are unique. It was possible because of the improved accuracy of our technique as compared to the pendant drop technique. In terms of the theory, the values of $\tilde{\kappa}_{ii}$ ($\kappa_{11} = \kappa_{22} = 0.5$) used for the components were not optimized for this temperature. Considering that no adjustable parameters were used, the quantitative agreement for the 32000/770 blend is remarkably good. The inset in Figure 2 shows the surface tension for the 2600/770 blend sample of PDMS at 50 °C. The same values of $\tilde{\kappa}_{ij}$ were used as for the first blend. The trend is correct but the agreement is not as good because of the shift in the end point value for the M_n = 2600 sample. This error is simply a measure of the scatter which results from experimental determination of the density for the *PVT* data. The strong negative deviation of the theory from that expected for a simple ideal additive behavior implies that there is surface segregation of the lower molecular weight component. This can be clearly seen in Figure 3, where the surface density profiles of the components are plotted for a composition of 30 wt % of

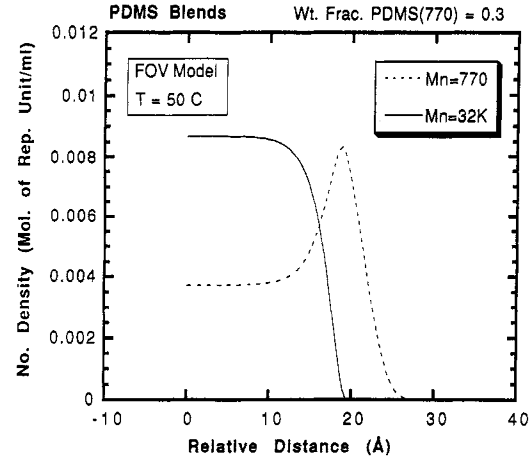

Figure 3. Density as a function of relative position for the two PDMS components (Mn = 32 000 and M_n = 770) at T = 50 °C and weight fraction of the low molecular weight component of 0.3.

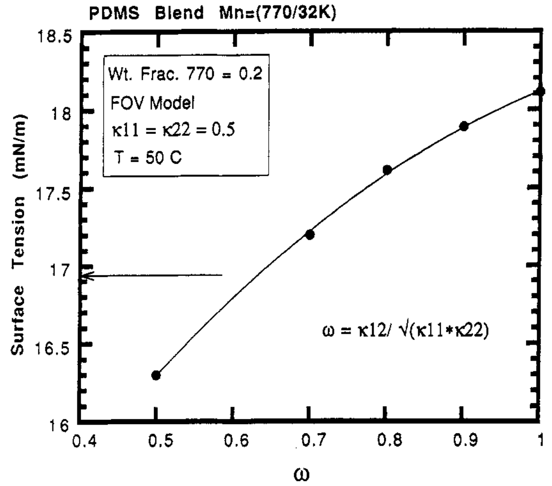

Figure 4. Surface tension as a function of ω for the PDMS blend at T = 50 °C and weight fraction of the low molecular weight component of 0.2 (see text).

the low molecular weight component at T = 50 °C. The lower surface energy component, which in this case happens to be the lower molecular weight component, is observed to be in excess at the liquid–vapor interface.

The good agreement between theory and experiment affords us the opportunity of studying the sensitivity of the results to the parameter $\tilde{\kappa}_{12}$. The value of X_{12} is assumed to be given by eq 15, which assumes random mixing. What is the effect of varying $\tilde{\kappa}_{12}$ for fixed X_{12}? Figure 4 shows the dependence of γ on the parameter $\omega = \tilde{\kappa}_{12}/(\tilde{\kappa}_{11}\tilde{\kappa}_{22})^{1/2}$ for a 20 wt % blend composition of the $\bar{M}_n$ = 770 PDMS component at T = 50 °C. For values of $\tilde{\kappa}_{12}$ equal to $0.6(\tilde{\kappa}_{11}\tilde{\kappa}_{22})^{1/2}$, the theoretical prediction drops below the experimental value for the pure M_n = 770 PDMS component which is indicated by the arrow. This is physically unrealistic. Values of $\tilde{\kappa}_{12} > (\tilde{\kappa}_{11}\tilde{\kappa}_{22})^{1/2}$, i.e., $\omega >$ 1, lead to unstable surface profiles. Figure 5 shows the surface profiles for the M_n = 770 PDMS sample at a 20 wt % composition for the values of ω = 1, 0.8, and 0.5. While the density of the blend drops from its bulk value to that of the vapor over a 15-Å region, the region over which the change in the relative amounts of the two components occurs increases with decreasing ω. For ω = 0.5, the region over which the low-M_n PDMS changes is on the order of 40–50 Å. The fact that ω = 1 agrees well with the experimental values is consistent with similar studies for low molecular weight liquid blends.[19]

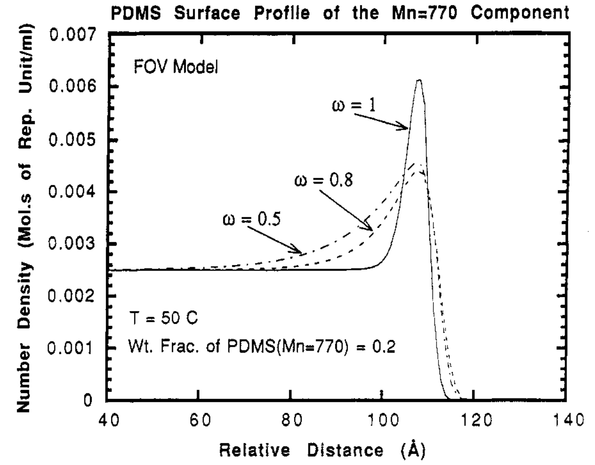

Figure 5. Density profile as a function of relative distance for the PDMS(M_n = 770) sample for values of ω = 1, 0.8, and 0.5.

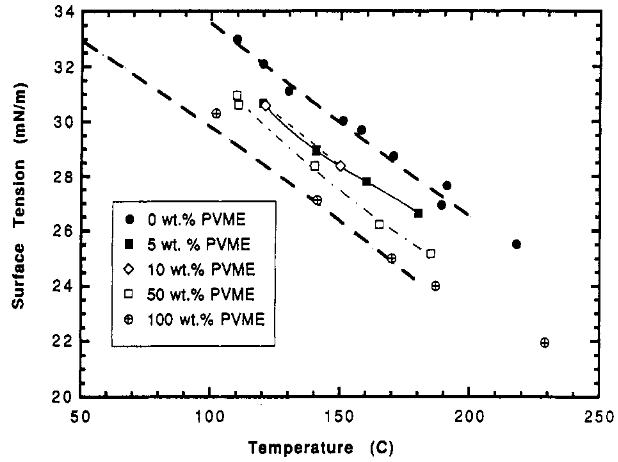

Figure 6. Surface tension as a function of temperature for PS, PVME, and the blends with 5, 10, and 50 wt % of PVME. The broad dashed lines through the PS and PVME data are theoretical predictions using values of k = 0.48 and 0.5, respectively.

PS–PVME Blends. We next consider a blend which we know to have a specific interaction which is responsible for the miscibility observed with this mixture at high molecular weights. Under these circumstances we must expect the random mixing approximation to be poor. The questions of interest are, (a) in the case where we use no adjustable parameters, can we predict the surface tension of the blend, and (b) if we cannot predict the quantitative details, what it the least adjustment to the model that we have to make to achieve quantitative agreement?

Blends of PS and PVME are miscible at the temperatures and molecular weights studied. Figure 6 shows the experimental measurements of the surface tensions of the pure components and the blends as a function of temperature. The experimental values for 100% PVME are significantly higher than those obtained by Bhatia et al.[20] Bulk density values for the blend compositions, which are critical in the pendant drop analysis of γ, were not measured in that report. Therefore, a comparison of the blend surface tensions presented here and previously[20] is not possible. The curves through the 100% PS and 100% PVME data in Figure 6 represent the theoretical fits to the data using values of $\tilde{\kappa}$ = 0.48 for PS and $\tilde{\kappa}$ = 0.5 for PVME. Figure 7 shows the surface tension as a function of composition at T = 150 °C for this blend. The value of ω was set equal to 1. The value of X_{12} was first set to its random mixing value; i.e., d_{12} = 1. This gives the lower curve in Figure 7, which has the correct qualitative features

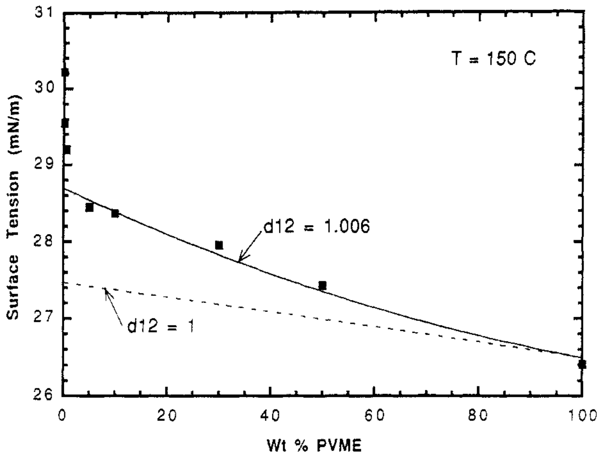

Figure 7. Surface tension as a function of the weight fraction of PVME at T = 150 °C. The theoretical curves for values of d_{12} of 1 and 1.006 are also shown (see text).

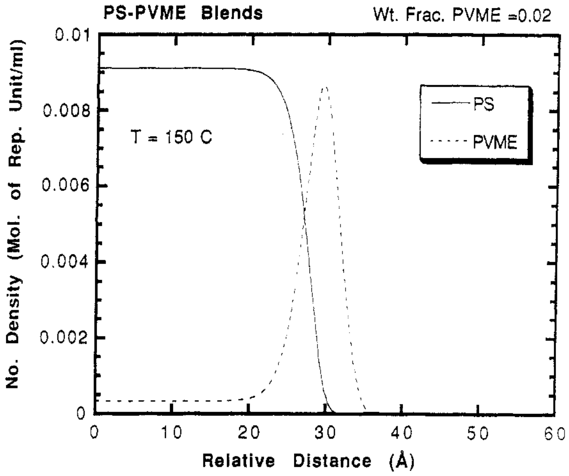

Figure 8. Surface profiles of the PS and PVME components at T = 150 °C and weight fraction of the PVME component of 0.02.

but is lower than the experimental observations. Using no adjustable parameters, very strong surface segregation is indicated by the strong negative deviation. The PS–PVME system is known to have an attractive specific interaction which gives rise to miscibility in these polymers. To mimic this interaction we can adjust the value of X_{12} so that it is attractive (a negative value). A value of X_{12} = −5.5 J/mL results for a value of d_{12} = 1.006. This results in very good agreement with the experimental data (Figure 7). The values of X_{12} = −5.5 J/mL, while not identical, is similar to the values necessary to model the phase diagrams of this system at higher molecular weights.[12]

Figure 8 shows the surface profiles of this system at a concentration of 2 wt % PVME. As expected, we observe a strong surface excess of PVME. The typical range over which the density changes at the interface is on the order of 15 Å. In this case the range over which the PVME deviates from its bulk concentration is also on the order of 15 Å. The present model ignores the polymer character of the PVME in that no information on the configurational entropy of the PVME molecule is taken into account. The confinement of the PVME to a narrow region near the surface implies an entropic penalty; i.e., the polymer would prefer to adopt a random walk configuration in three dimensions. If this entropic cost is much smaller than the enthalpic gain, which is taken into account by the model, then the confinement of the PVME molecules to this narrow region is possible. In our previous work[1] on single-component liquids, we demonstrated that the contribution of the configurational entropy of polymers to the surface tension is negligibly small. The existing experimental evidence[20] suggests that the PVME is not as confined as the model suggests. Further work is necessary in this area to establish the nature of the PVME density profile at the liquid–vapor interface of this blend.

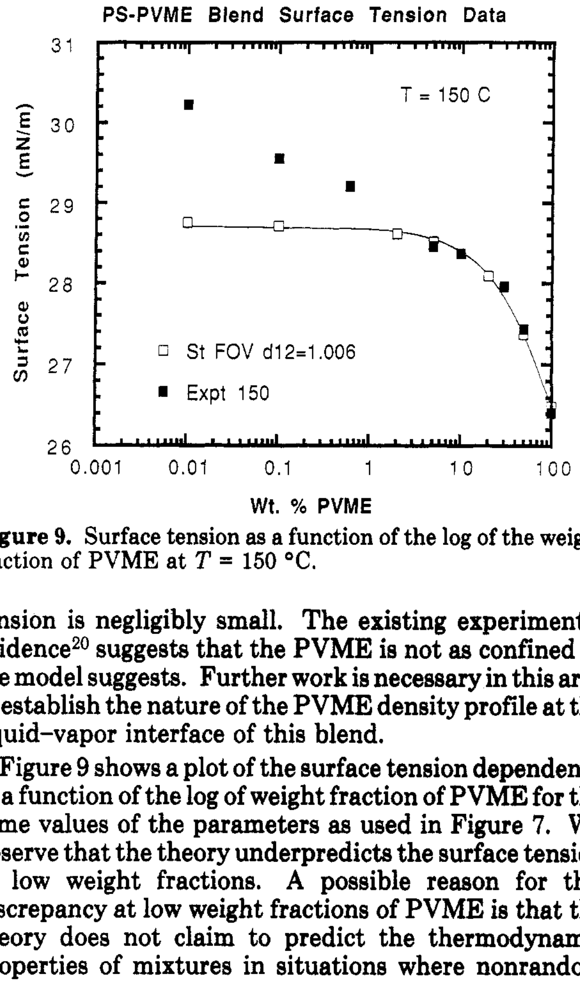

Figure 9. Surface tension as a function of the log of the weight fraction of PVME at T = 150 °C.

Figure 9 shows a plot of the surface tension dependence as a function of the log of weight fraction of PVME for the same values of the parameters as used in Figure 7. We observe that the theory underpredicts the surface tension at low weight fractions. A possible reason for this discrepancy at low weight fractions of PVME is that the theory does not claim to predict the thermodynamic properties of mixtures in situations where nonrandom mixing occurs. There may be a concentration dependence of the interaction parameter X_{12} over and above the equation of state contributions taken into account by the theory. Another possibility is that the Flory–Huggins entropy of mixing is incorrect in predicting the behavior of the blend at low weight fractions of the polymer component. To investigate the sensitivity of the surface tension to the expression for the entropy of mixing in the bulk, we ran simulations where we varied the molecular weight of the PVME but did not adjust the reduction parameters which describe the thermodynamic properties of the PVME. In the low weight fraction region the predicted and experimental results could be made to agree by inputting theoretical values of M_n in the range of 5000 g/mol. In the range of concentrations from 10 to 50 wt % PVME the predicted surface tensions were above the experimental results by about 0.2 mN/m as a result of this procedure. The real cause of the discrepancy may be a combination of the many shortcomings of the mixing rules for the blend when nonrandom mixing occurs.

Conclusions

Using only PVT data for the pure components, we can predict surface properties of miscible blends. In the case of the PDMS blends of different molecular weights for example, the theory describes the surface properties of the mixture quantitatively. The results suggest that there is a strong surface excess of the low molecular weight component. We conclude that in mixtures where random mixing of the components occurs, we can expect the theory to describe the mixture properties with no adjustable parameters. The theory should have very useful applications in the description of the surface properties of a polydisperse polymer sample with a number-average molecular weight in the range 500–5000. Another application is to polymers with bimodal distributions where one of the components is a low molecular weight component.

In cases where deviations from random mixing occur one can still model the surface tension by using physically reasonable mixture parameters. In the case of the PS/PVME blends we know that a specific interaction exists which accounts for the miscibility of this mixture. It is not surprising therefore that we need to include a favorable bulk interaction between the polymers to achieve agreement between theory and experiment. At low weight fractions of PVME the theory shows deviations from the experimental results. Therefore, we must conclude that in blends where miscibility results from the presence of attractive interactions we must expect the predictive power of this theory to be limited.

Nonzero κ_{12} should be used to model the surface and interfacial tension of polymer blends. We demonstrated that the appropriate value of the coefficient κ_{12} is close to that specified by the geometric mean of the coefficients of the pure components to the mixture. This is in agreement with previous results for low molecular weight liquid mixtures. Although arguments have been presented that the value of κ_{12} should be close to zero for polymer blends, for the calculation of interfacial tensions we can find no rigorous justification for this assumption. We argue that the geometric mean should be used for both the case of surface and interfacial tension calculations.

We will next turn our attention to the prediction of interfacial tension using the above theory in conjunction with *PVT* data. In situations where there are sizeable density differences between the two phases, we expect nontrivial equation of state contributions to the interfacial tension which should be predicted by this theory. In cases where such contributions are small we expect the theory to fail as contributions from the conformational entropy of polymers at the interface will be important and are not included in the present theory.

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Appendix 1

Mixtures in the FOV Equation of State Formalism. Consider a mixture contaiing N_1 molecules of the first component and N_2 molecules of the second. The two components are characterized by their reduction parameters P^*_i, T^*_i, and V^*_i, where $i = 1, 2$. If $N = N_1 + N_2$ is the total number of molecules in the system, r_1 and r_2 are the number of mers per molecule of the respective components, c_1 and c_2 are the number of effective degrees of freedom per mer for each component, and s_1 and s_2 are the number of nearest-neighbor contacts of the mers of the respective components, then we define the following quantities:

$$x_1 \equiv N_1/N = 1 - x_2 \tag{A.1}$$

$$r \equiv x_1 r_1 + x_2 r_2 \tag{A.2}$$

$$\phi_1 \equiv r_1 N_1/rN = 1 - \phi_2 \tag{A.3}$$

$$s \equiv \phi_1 s_1 + \phi_2 x_2 \tag{A.4}$$

$$c \equiv \phi_1 c_1 + \phi_2 c_2 \tag{A.5}$$

i.e., x_1 is the mole fraction and ϕ_1 is the site fraction of component 1. With these definitions we define the following rules which we will use fo the mixture.

(a) The hard-core mer volumes are defined to be equal:

$$v^*_1 = v^*_2 = v^* \tag{A.6}$$

(b) The hard-core volume of the mixture, V^*, is equal to the sum of the hard core volumes of the components:

$$V^* = rNv^* \tag{A.7}$$

(c) The number of pair interactions in the mixture is equal to the sum of the pure component pair interactions; i.e., if N_{ij} is the number of i,j pair interactions, then

$$N_{11} + N_{12} + N_{22} = (s_1 r_1 N_1 + s_2 r_2 N_2)/2 = srN/2 \tag{A.8}$$

With the above definitions and rules, the partition function for the mixture can be written in the form

$$Z_N = Z_{\mathrm{comb}}(\lambda^{-1} g(v^{1/3} - v_{\mathrm{hc}}{}^{1/3}))^{3(c_1 r_1 n_1 + c_2 r_2 n_2)} \exp(-E_0/kT) \tag{A.9}$$

where λ represents the contribution to the partition function from the translational degrees of freedom of mers of effective mass m_{eff} which are assumed to be classical. The hard core cell volume $v_{\mathrm{hc}} = \gamma v^*$, where γ is a geometrical factor related to the choice of the geometry of the cells. Z_{comb} is the Flory–Huggins combinatorial entropy, which is of the form such that

$$\ln Z_{\mathrm{comb}} = N_1 \ln \phi_1 + N_2 \ln \phi_2 \tag{A.10}$$

In evaluating the free volume term we have used the square well approximation for the cell potential. The function $E_0(V)$ is the interaction energy computed when all the mers are at their cell centers, and for mixtures it is of the form

$$-E_0(V) = (N_{11}\eta_{11} + N_{12}\eta_{12} + N_{22}\eta_{22})\psi(v) \tag{A.11}$$

where η_{ij} is the characteristic energy of interaction between mers of component i and j and $\psi(v)$ is the interaction potential. For the FOV model, $\psi(v)$ is of the form

$$\psi(v) = -2v^*/v \boxminus -2/\tilde{v} \tag{A.12}$$

If random mixing of the two mers is assumed, then

$$N_{11} = {}^1/_2(s_1 r_1 N_1 \vartheta_1), \qquad N_{22} = {}^1/_2(s_2 r_2 N_2 \vartheta_2), \qquad N_{12} = s_1 r_1 N_1 \vartheta_2 \tag{A.13}$$

where $\vartheta_1 = s_1 r_1/srN = 1 - \vartheta_2$. Using these definitions, we can write

$$-E_0/rN = {}^1/_2(\vartheta_1\epsilon_1 + \vartheta_2\epsilon_2 - s_1\vartheta_1\vartheta_2\Delta\eta) \tag{A.14}$$

where $\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12}$ and $\epsilon_i = s_i\eta_{ii}$. If we define an interaction parameter X_{12} so that

$$X_{12} \equiv s_1\Delta\eta/v^* \tag{A.15}$$

then eq A.11 becomes

$$-E_0/rN = 2(\epsilon_1\phi_1 + \epsilon_2\phi_2 - v^* X_{12}\phi_1\vartheta_2)\psi(v) \equiv 2\epsilon\psi(v) \tag{A.16}$$

Since P^* and T^* are defined as

$$P^* = \epsilon/v^* \qquad T^* = \epsilon/ck$$

eq A.16 leads to a definition of P^* and T^* for the mixture of the form

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - X_{12}\phi_1\vartheta_2 \tag{A.17}$$

$$T^* = P^*/[\phi_1(P^*_1/T^*_1) + \phi_2(P^*_2/T^*_2)] \tag{A.18}$$

Finally, if we define $\tilde{P} = P/P^*$ and $\tilde{T} = T/T^*$, the partition function can be written in the form

$$Z_N = \alpha v^{*crN} Z_{\text{comb}} [(\tilde{v}^{1/3} - \gamma^{1/3})^{3c} \exp(-2c\psi(\tilde{v})/\tilde{T})]^{Nr} \tag{A.19}$$

where we have excluded the contribution from the translational degrees of freedom. From eq A.19 we can extract the expression for the Gibbs free energy of the mixture, which has the following form:

$$G = PV + \epsilon^* rN\{-1/\tilde{v} - \tilde{T}[\ln(v^*) + 3 \ln (\tilde{v}^{1/3} - 1)] + (T/c)[(\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2]\} \tag{A.20}$$

The chemical potential can be computed using the following expression

$$\mu_1 = kT\partial(\ln Z_N)/\partial N_1|_{T,V,N_2} \tag{A.21}$$

with a similar expression for μ_2.

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