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Modeling Osmotic Pressure Second Virial and Preferential Adsorption Coefficient Data of Ternary Solvent–Polymer–Solvent Systems Using Equation-of-State Solution Theories

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ABSTRACT: Three equation-of-state (EOS) solution theories have been applied to binary and ternary solvent–polymer–solvent data at infinite dilution of the polymer. The data, from light scattering, osmotic pressure, and sedimentation equilibrium experiments, were taken from literature and were in the form of the osmotic pressure second virial coefficient of the solvent and the preferential adsorption coefficient of the polymer. The systems studied were the binary benzene–polystyrene and cyclohexane–polystyrene systems and the resulting ternary system, benzene–polystyrene–cyclohexane. A significant result is that the solution theory interaction parameter values obtained for the binary solvent–polymer system in the infinitely dilute polymer regime using these data are consistent with parameters at the other extreme (polymer-rich) and obtained by different experiments. For the ternary system, the three EOS solution theories were able to model the osmotic pressure second virial coefficient, and, using the same model parameters, they had reasonable success at modeling the preferential adsorption coefficient. For the Flory EOS model, the solvent–solvent binary parameter estimated with the ternary data matched that obtained from binary solvent–solvent VLE data and the solvent/polymer segment–surface ratios estimated with the ternary data matched the average of the geometric and group contribution values.

Introduction

Polymer solution theories provide physically reasonable models with which to describe the thermodynamic behavior of polymer–solvent systems with a small number of adjustable fit parameters. In addition, equation-of-state (EOS) solution theories can be used to generate phase equilibrium data at solution compositions not studied experimentally and to predict other thermodynamic behavior such as mixture miscibility limits, i.e., binodals, spinodals, and critical solution temperatures.

Yet, EOS models have experienced limited testing and application, partly due to the complexity of the equations, especially for ternary or higher multicomponent systems. Work has been done at infinite dilution of the solvent in polymer and at finite concentrations in the polymer-rich region by gas chromatography and static measurements.[1] However, little is known about the applicability of these theories to the dilute polymer region, which offers unique challenges to the theories. Researchers have tended to use variations of the classical Flory–Huggins lattice theory, usually extended for ternary systems by introducing parameters that represent free energies associated with ternary interactions.

From another perspective, multicomponent phenomena in the dilute polymer regime are in need of improved models with physically interpretable parameters. Limited success has been realized in representing and understanding the complex behavior of cosolvent systems as manifested by the osmotic pressure second virial coefficient and the preferential adsorption coefficient.

The objective of this study was to obtain the relations for the second virial and preferential adsorption coefficients using several multicomponent EOS polymer solution theories and then to extract the binary interaction parameters for the theories by means of a parameter estimation procedure using second virial coefficient and preferential adsorption coefficient literature data. In this approach the parameters were treated as constants, independent of concentration.

One of the problems in modeling dilute polymer solutions is the excluded volume, the notion that at infinite dilution of polymer the solution is no longer homogeneous but rather is better described as individual polymer molecules having adsorbed solvent, each occupying its own volume in a sea of pure solvent (or solvent mixture) which effectively excludes other polymer molecules.[2,3] This effect is manifested by a dependence of the second virial coefficient on polymer molecular weight, except at the Θ temperature for the polymer where the excluded volume (and hence the second virial coefficient) is zero for all molecular weights.[4]

Previous approaches to modeling the dilute polymer regime have, for the most part, followed one of two approaches concerning the excluded volume. Either they have followed the lead of Flory and co-workers and explicitly represented the excluded volume through the integral $F(X)$ in calculating the model parameters, or they have omitted this integral, thereby requiring the model parameters to incorporate the effects of excluded volume. In this latter approach, the extent to which the parameters vary with molecular weight may be viewed as an indication of how well the model otherwise handles the excluded volume effect. In this work, we follow this latter approach.

Previous Modeling Efforts. Most previous approaches to describing dilute polymer solutions have used variations of the Flory–Huggins model. Early work on models for binary polymer–solvent systems related A_2 to χ,[5] introduced the excluded volume correction to account for the variation in A_2 with molecular weight,[2,3] and allowed for concentration dependence in χ by adding higher order terms.[6] Extensions to ternary polymer–two-solvent systems also were introduced.[7,8]

To improve the ternary models that incorporated only binary interaction parameters, Read[9] introduced terms representing ternary interactions and applied this model to preferential adsorption data. Interaction parameters representing the solvent (1)–polymer (2)–polymer (2), solvent (3)–polymer (2)–polymer (2), and solvent (1)–polymer (2)–solvent (3) interactions were added. The two solvent–polymer–polymer ternary interaction parameters, along with the three binary interaction parameters, were extracted from data for the respective binary systems. Then the solvent (1)–polymer (2)–solvent (3) ternary interaction parameter was estimated with the ternary data. Six parameters were used in this approach for the ternary

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system. Overall sorption was not evaluated in this work.

Pouchlý et al.[10] obtained expressions for the overall and preferential adsorption in two-solvent systems which were general and cast in terms of partial derivatives obtained from the free enthalpy of mixing. They then applied these expressions to a Flory–Huggins ternary model containing a single ternary parameter, one that represents interactions between all three species. They applied the theory to the benzene–poly(methyl methacrylate)–methanol system in the following way. The solvent–solvent binary parameter, as a function of solvent mixture concentration, was obtained from independent VLE data given by the Redlich–Kister equation with constants from Scatchard and Ticknor[11] and fit to a quadratic function of solvent concentration. The ternary parameter was found to depend on both the solvent and polymer concentrations; a total of four fit parameters was required to relate this interaction parameter to composition. The two solvent–polymer interaction parameters were found to be linear with respect to the polymer concentration. A total of eleven fit parameters, four estimated with the ternary data, was required for this formulation of this system. These produced reasonable agreement with the data, although significant deviation in the shape of the Y function of Schultz and Flory[8] was evident. The excluded volume effect was not considered.

In work specifically on the benzene–polystyrene–cyclohexane system, Pouchlý and Živný[12] again used this eleven-parameter model, with four parameters estimated from a fit of ternary preferential adsorption data. A good representation of the data was obtained.

Dondos and Patterson[13] applied this same theory to intrinsic viscosity data for several solvent–polymer–solvent systems, again using a Flory–Huggins ternary model containing a ternary interaction parameter. They obtained reasonable qualitative but poor quantitative agreement of the theory with experimental data.

Chu and Munk consider two approaches to modeling dilute polymer solutions,[14,15] For binary systems, they divided interaction functions into two parts: a molecular weight independent part and a part representing excluded volume effects. They considered this in combination with the theory of Koningsveld et al.[16] They reported qualitative but not quantitative agreement between theory and experiment. In a second approach, they use a Flory–Huggins type expression for the Gibbs free energy of mixing which includes a ternary interaction term. The interaction energy functions are considered to be functions of composition, and the data analysis procedure provides a numerical determination of the ternary function which satisfies both second virial and preferential adsorption data. The solvent–solvent function was obtained from solvent–solvent VLE using a representation that was quadratic in volume fraction. Although the ternary parameter that they obtained is a complex function of composition and not readily interpreted, they concluded that the necessity of introducing a ternary function was established. In neither approach did they consider the free volume effect.

More recently, Horta[17] departed from the approach of introducing a ternary interaction term by evaluating a modified Flory–Prigogine–Patterson (FPP) EOS theory.[18] He derived relationships for both the preferential adsorption and the second virial coefficients based on this theory which was first applied to polymers in mixed solvents by Pouchlý and Patterson.[19]

Although the derivatives by Horta and Pouchlý and Patterson were based on the complete theory, the simplifications that were made omitted some of its useful features. For his derivation, Horta assumed, as did Pouchlý and Patterson, that the differences between the two solvents were negligible compared to the polymer–solvent differences. This led to a single-liquid approximation where the binary solvent mixture was assumed to be a single solvent with properties corresponding to the average of the two solvents. At infinite dilution of the polymer, this approximation circumvented the theory's equation of state. The above simplifications were made by Horta to "find a form more amenable to calculation."[17] The formulation for the second viral coefficient was further simplified in accordance with the work of Pouchlý and Patterson,[19] which neglected the preferential adsorption term as part of a single-liquid approximation for the total sorption. The final form of Horta's formulation retained free volume dissimilarity and surface-to-volume ratio terms.

In the implementation of this theory, whereas the binary interaction parameters have been determined with binary data, the segment–surface ratio has been variously estimated. First was an á priori calculation from the molecular geometry of the solvent and polymer. Second was a parameter estimation procedure that treated the ratio as a function of composition containing adjustable parameters. Constant, linear, and quadratic functions have been considered.[20-22] For the benzene–polystyrene–cyclohexane system, they found that an eight-parameter model containing constant polymer–solvent parameters and representations for both the solvent–solvent parameter and the segment–surface ratio that were quadratic in cyclohexane volume fraction in the solvent mixture represented the data. Three of these parameters, those for the segment–surface ratio, were estimated from the ternary preferential adsorption data.[21] A significant conclusion from this work using the FPP theory is that ternary system behavior can be described by considering only the binary interactions without resorting to ternary interaction terms.[20]

Still more recently, Horta[23] presented equations for the FPP theory that are based upon his earlier work[17] but that do not make the single-liquid approximation, in an effort to implement a full EOS theory. He cast his equations into a form paralleling the ternary Flory–Huggins equations for the purpose of interpreting the ternary term in the context of the FPP EOS theory. Calculations showed that segment–surface ratios and free volume dissimilarities can account for a significant part of this ternary Flory–Huggins parameter.

Procedure

Thermodynamic relations for osmotic pressure second virial coefficients and preferential adsorption coefficients in terms of species activities, along with the solution theory equations for species activities, provide the basis for calculating the second virial and preferential adsorption coefficients. Comparing these calculations with experimental data allows optimally selecting or estimating the solution theory interaction parameters. In addition to these relations and the data, pure component parameters and (for the Flory theory) segment–surface ratios are required. In the Flory theory, the segment–surface ratios also can be treated as adjustable parameters and selected with the ternary data. The methodology and procedure for these calculations are presented below.

Thermodynamic Relationships. Stockmayer[24] derived a multicomponent thermodynamic relationship for light scattering in dilute polymer solutions using Einstein's equation for a multicomponent, nonelectrolyte system. With the assumption of constant pressure, temperature,

and chemical potentials of the components, the fluctuations in the volume and concentrations are described by a modified grand canonical ensemble.

For binary solvent (1)–polymer (2)–solvent (3) systems, Stockmayer's derivation gives the osmotic pressure second virial coefficient of the solvent as

$$A_2 = \left[\left(\frac{\partial \ln a_2}{\partial n_2}\right)_{T,P,n_1} - \frac{1}{n_2}\right]\frac{n_2}{2CM_2} \quad (1)$$

or, when the polymer is at infinite dilution, $C = n_2M_2/(r_1n_1v_1)$ so that

$$A_2 = \left[\left(\frac{\partial \ln a_2}{\partial n_2}\right)_{T,P,n_1} - \frac{1}{n_2}\right]\frac{n_1v_{1sp}^*\tilde{v}_1M_1}{2M_2^2} \quad (2)$$

The term $1/n_2$ cancels a like term that arises from $(\partial \ln a_2/\partial n_2)$ or, more specifically, from $(\partial \ln \psi_2/\partial n_2)$.

For ternary solvent (1)–polymer (2)–solvent (3) systems Stockmayer's formulation is limited to solutions at infinite dilution of the polymer. This limitation is introduced since the difference

$$\left(\frac{\partial \ln a_3}{\partial n_3}\right)_{T,P,n_1,n_2} - \left(\frac{\partial \ln a_3}{\partial n_3}\right)_{T,P,n_1,n_2=0} \quad (3)$$

is required to be zero for Stockmayer's relationship to correspond to experimental relationships. Stockmayer's derivation for ternary systems at infinite dilution of the polymer gives

$$\lambda = -\left[\left(\frac{\partial \ln a_3}{\partial n_2}\right)_{T,P,n_1,n_3}\right]\left[\left(\frac{\partial \ln a_3}{\partial n_3}\right)^{-1}_{T,P,n_1,n_2}\right] \times \left(\frac{\partial n}{\partial C}\right)_{T,P,\phi_1}\left[\left(\frac{\partial n}{\partial \phi_1}\right)^{-1}_{T,P,C}\right]\left[\left(\frac{\partial n}{\partial n_3}\right)_{T,P,n_1,n_2}\right] \times \left[\left(\frac{\partial n}{\partial n_2}\right)^{-1}_{T,P,n_1,n_3}\right] \quad (4)$$

Writing $n = n(T,P,C,\phi_1)$ and using the relations $(\partial\phi_1/\partial n_2)_{T,P,n_1,n_3} \equiv 0$ (ϕ_1 is defined on a polymer-free basis) and $(\partial C/\partial n_3)_{T,P,n_1,n_3} = 0$ at infinite dilution of polymer ($n_2 = 0$) give

$$\left(\frac{\partial n}{\partial n_2}\right)_{T,P,n_1,n_3} = \left[\left(\frac{\partial n}{\partial C}\right)_{T,P,\phi_1}\right]\left[\left(\frac{\partial C}{\partial n_2}\right)_{T,P,n_1,n_3}\right]$$

and

$$\left(\frac{\partial n}{\partial n_3}\right)_{T,P,n_1,n_2} = \left[\left(\frac{\partial n}{\partial \phi_1}\right)_{T,P,C}\right]\left[\left(\frac{\partial \phi_1}{\partial n_3}\right)_{T,P,n_1,n_2}\right]$$

and hence, in eq 4

$$\left[\left(\frac{\partial n}{\partial C}\right)_{T,P,\phi_1}\right]\left[\left(\frac{\partial n}{\partial \phi_1}\right)^{-1}_{T,P,C}\right]\left[\left(\frac{\partial n}{\partial n_3}\right)_{T,P,n_1,n_2}\right] \times \left[\left(\frac{\partial n}{\partial n_2}\right)^{-1}_{T,P,n_1,n_3}\right] = \left[\left(\frac{\partial C}{\partial n_2}\right)^{-1}_{T,P,n_1,n_3}\right]\left[\left(\frac{\partial \phi_1}{\partial n_3}\right)_{T,P,n_1,n_2}\right] \quad (5)$$

The actual working form for eq 4 then is

$$\lambda = \frac{\phi_1\phi_3\tilde{v}(M_1v_{1sp}^*n_1 + M_3v_{3sp}^*n_3)}{M_2n_3} \times \left[n_3\left(\frac{\partial \ln a_3}{\partial n_2}\right)_{T,P,n_1,n_3}\right]\left[n_3\left(\frac{\partial \ln a_3}{\partial n_3}\right)^{-1}_{T,P,n_1,n_2}\right] \quad (6)$$

Stockmayer's derivation also gives

$$A_{2,M} = \frac{n_2}{2CM_2}\left\{\left[\left(\frac{\partial \ln a_2}{\partial n_2}\right)_{T,P,n_1,n_3}\right] - \frac{1}{n_2} - \left[\left(\frac{\partial \ln a_3}{\partial n_2}\right)^2_{T,P,n_1,n_3}\right]\left[\left(\frac{\partial \ln a_3}{\partial n_3}\right)^{-1}_{T,P,n_1,n_2}\right]\right\} \quad (7)$$

where $A_{2,M}$ is the osmotic pressure second virial coefficient of the solvent mixture. The working equation for this result is

$$A_{2,M} = \frac{v_{2sp}^*\tilde{v}}{2M_2}\left\{\frac{n_2}{\psi_2}\left[\left(\frac{\partial \ln a_2}{\partial n_2}\right) - \frac{1}{n_2}\right]\right\} - \frac{\tilde{v}(M_1v_{1sp}^*n_1 + M_3v_{3sp}^*n_3)}{2n_3M_2^2}\left\{\left[n_3\left(\frac{\partial \ln a_3}{\partial n_2}\right)\right]^2 \times \left[n_3\left(\frac{\partial \ln a_3}{\partial n_3}\right)\right]^{-1}\right\} \quad (8)$$

These working equations, although originating in the light scattering method, retain no quantity that is specific to light scattering and can be used for second virial and preferential adsorption data obtained from other methods, as well, such as sedimentation equilibrium. With the use of a solution theory equation for the activities, values of A_2, λ, and $A_{2,M}$ can be calculated for comparison with experimental data.

Polymer Solution Theories. For this work, three polymer solution theories were used to provide representations of the activities of components in a mixture as a function of temperature, pressure, and composition. They are the Flory theory,[25] based on the work of Prigogine,[26,27] the simplified Flory theory,[28,29] and the Sanchez and Lacombe lattice fluid theory.[30] The multicomponent forms of the three EOS solution theories are presented in Tables I and II.[31]

This choice of theories provides a variety of means for accounting for species free volume and surface contact area dissimilarities. All three theories account for free volume dissimilarities among the species. In addition, the Flory theory explicitly provides for surface contact area dissimilarities through the s parameter. The simplified Flory theory eliminates this feature by setting all s values to unity, thus gaining some simplifications in computation. The lattice fluid theory does not provide for surface contact dissimilarity in an explicit manner but rather does so implicitly through mixing rules.[30]

The solution theories are applied to second virial coefficient and preferential adsorption coefficient data through eq 2, 6, and 8. These equations require the derivative

$$\left(\frac{\partial \ln a_i}{\partial n_j}\right)_{T,P,n_{k\neq j}} \quad (9)$$

in either a binary or ternary form. The equation for the general multicomponent composition derivative of the activity was derived for each theory, and these equations are presented in Tables III and IV.

These derivative equations for the solution theories were checked by comparing their calculations with each other and with calculations using the Redlich–Kister equations for vapor-phase activities in terms of liquid-phase mole fractions. All calculations were for benzene–cyclohexane VLE at 298 K. Parameters for this system for the Redlich–Kister equations were obtained from Li et al.[32] Derivative equations were obtained by differentiating the Redlich–Kister equations with respect to moles. With these parameters and the derivative equations, derivative values were calculated over the range of composition.

Table I
Solution Model Equations

model	solution activity (a_i)
Flory[a,d]	$\psi_i \exp\left\{\sum_j\left(1-\frac{r_i}{r_j}\right)\psi_j + \frac{M_i v_{isp}^*}{RT}\left[P_i^*\left(3\tilde{T}_i \ln\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}^{1/3}-1} + \tilde{p}_i - \tilde{p} + \tilde{P}_i(\tilde{v}-\tilde{v}_i)\right) - \tilde{p}\sum_{j=1}^{m-1}\sum_{k=j+1}^{m}\theta_j\frac{s_i}{s_j}X_{jk}\theta_k + \tilde{p}\sum_j\theta_j X_{ij}\right]\right\}$
simplified Flory[b,d]	$\psi_i \exp\left\{\sum_j\left(1-\frac{r_i}{r_j}\right)\psi_j + \frac{M_i v_{isp}^*}{RT}\left[P_i^*\left(3\tilde{T}_i \ln\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}^{1/3}-1} + \tilde{p}_i - \tilde{p} + \tilde{P}_i(\tilde{v}-\tilde{v}_i)\right) + \tilde{p}\sum_j\sum_k\psi_j P_{jk}^*\psi_k - 2\tilde{p}\sum_j\psi_j P_{ji}^*\right]\right\}$
lattice fluid[c,d]	$\psi_i \exp\left\{\sum_j\left(1-\frac{r_i}{r_j}\right)\psi_j + \frac{M_i v_{isp}^*}{RT}\left[P_i^*(\tilde{p}_i - \tilde{p} + \tilde{P}_i(\tilde{v}-\tilde{v}_i) + \tilde{T}_i[(\tilde{v}-1)\ln(1-\tilde{p}) - (\tilde{v}_i-1)\ln(1-\tilde{p}_i)]) - \frac{\tilde{p}}{2}\sum_j\sum_k\psi_j\Delta P_{jk}^*\psi_k + \tilde{p}\sum_j\psi_j\Delta P_{ji}^*\right] + \ln\frac{\tilde{p}}{\tilde{p}_i}\right\}$

[a] $X_{ij} = \frac{s_i}{s_j}X_{ji}$; $\frac{r_i}{r_j} = \frac{M_i v_{isp}^*}{M_j v_{jsp}^*}$; $\theta_j = \frac{\psi_j}{\sum_k \frac{s_k}{s_j}}$; $X_{ii} = 0$. [b] $P_{ij}^* = P_{ji}^*$; $P_{ii}^* = P_i^*$. [c] $\Delta P_{ij}^* = P_i^* + P_j^* - 2P_{ij}^*$; $\Delta P_{ii}^* = 0$; $\frac{r_i}{r_j} = \frac{M_i v_{isp}^*}{M_j v_{jsp}^*}$. [d] Summations are from 1 to m unless otherwise indicated.

Table II
Mixture Rules and Equations of State

model[a]	mixture rules[b]	equation of state[c]
Flory	$P^* = \sum_i\psi_i P_i^* - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m}\psi_i X_{ij}\theta_j$ $T^* = P^*\left[\sum_i\psi_i\frac{P_i^*}{T_i^*}\right]^{-1}$	$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{v}\tilde{T}}$
simplified Flory	$P^* = \sum_i\sum_j\psi_i\psi_j P_{ij}^*$ $T^* = P^*\left[\sum_i\psi_i\frac{P_i^*}{T_i^*}\right]^{-1}$	$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{v}\tilde{T}}$
lattice fluid	$P^* = \sum_i\psi_i P_i^* - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m}\psi_j\psi_i\Delta P_{ij}^*$ $T^* = P^*\sum_i\frac{\psi_i^\circ T_i^*}{P_i^*}$	$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{r} - 1 - \tilde{v}\ln(1-\tilde{p}) - \frac{1}{\tilde{v}\tilde{T}}$

[a] See footnotes to Table I. [b] $\psi_i^\circ = \frac{\psi_i P_i^*}{T_i^*}\sum_j\frac{\psi_j^\circ T_j^*}{P_j^*}$. [c] $\frac{1}{r} = \sum_j\frac{\psi_j P_j^*}{r_j^\circ T_j^*}\sum_k\frac{\psi_k^\circ T_k^*}{P_k^*}$.

Table III
Solution Model Activity Composition Derivatives

model[a]	$(\partial \ln a_i/\partial n_j)_{T,P,n_{k\neq j}}$
Flory	$\frac{\delta_{ij}}{n_i} - \frac{\psi_j}{n_j}\left[\frac{r_i}{r_j} + \sum_k\psi_k\left(1-\frac{r_i}{r_k}\right)\right] + \frac{M_i v_{isp}^*}{RT\tilde{v}^2}\left[P_i^*\left(1 + \tilde{P}_i\tilde{v}^2 - \frac{\tilde{T}_i\tilde{v}^{4/3}}{\tilde{v}^{1/3}-1}\right) + \sum_{l=1}^{m-1}\sum_{k=l+1}^{m}\theta_l\frac{s_i}{s_l}X_{lk}\theta_k - \sum_k\theta_k X_{ik}\right]\frac{\partial\tilde{v}}{\partial n_j} + \frac{M_i v_{isp}^*}{RT\tilde{v}}\left(\frac{\theta_j}{n_j}\right)\left[X_{ij} - \sum_k X_{ik}\theta_k + 2\sum_{l=1}^{m-1}\sum_{k=l+1}^{m}\theta_l\frac{s_i}{s_l}X_{lk}\theta_k - \frac{1}{2}\frac{s_i}{s_j}\sum_k X_{jk}\theta_k - \frac{1}{2}\frac{\theta_i}{\psi_i}\sum_k X_{kj}\psi_k\right]$
simplified Flory	$\frac{\delta_{ij}}{n_i} - \frac{\psi_j}{n_j}\left[\frac{r_i}{r_j} + \sum_k\psi_k\left(1-\frac{r_i}{r_k}\right)\right] + \frac{M_i v_{isp}^*}{RT\tilde{v}^2}\left[P_i^*\left(\tilde{P}_i\tilde{v}^2 - \frac{\tilde{T}_i\tilde{v}^{4/3}}{\tilde{v}^{1/3}-1}\right) - \sum_l\sum_k\psi_l P_{lk}^*\psi_k + 2\sum_k\psi_k P_{ki}^*\right]\frac{\partial\tilde{v}}{\partial n_j} - \frac{M_i v_{isp}^*}{RT\tilde{v}}\frac{2\psi_j}{n_j}[P_{ij}^* - \sum_k P_{ki}^*\psi_k + \sum_l\sum_k\psi_l P_{lk}^*\psi_k - \sum_k P_{jk}^*\psi_k]$
lattice fluid	$\frac{\delta_{ij}}{n_i} - \frac{\psi_j}{n_j}\left[\frac{r_i}{r_j} + \sum_k\psi_k\left(1-\frac{r_i}{r_k}\right)\right] + \frac{M_i v_{isp}^*}{RT\tilde{v}^2}\left[P_i^*\left(1 + \tilde{P}_i\tilde{v}^2 + \tilde{v}^2\tilde{T}_i\left\{\ln(1-\tilde{p}) + \tilde{p}\left(1 - \frac{RT}{M_i v_{isp}^* P_i^*\tilde{T}_i}\right)\right\}\right) + \frac{1}{2}\sum_l\sum_k\psi_l\Delta P_{lk}^*\psi_k - \sum_k\psi_k\Delta P_{ki}^*\right]\frac{\partial\tilde{v}}{\partial n_j} + \frac{M_i v_{isp}^*\psi_j}{RT\tilde{v}}\frac{1}{n_j}[\Delta P_{ij}^* - \sum_k\Delta P_{ik}^*\psi_k + \sum_l\sum_k\psi_l\Delta P_{lk}^*\psi_k - \sum_k\Delta P_{jk}^*]$

[a] See footnotes to Table I.

Table IV
Solution Model Reduced Volume Composition Derivative

model[a]	$(\partial\tilde{v}/\partial n_j)_{T,P,n_{k\neq j}}$
Flory	$\left(\frac{\tilde{v}(\tilde{v}^{1/3}-1)}{\tilde{v}^{1/3}-\frac{4}{3}-\tilde{P}\tilde{v}^2(\tilde{v}^{1/3}-\frac{2}{3})}\right)\left(\frac{\psi_j}{n_j}\right)\left[(\tilde{P}\tilde{v}^2+1)\left(1-\frac{T^*P_i^*}{P^*T_j^*}\right)-1+\frac{1}{P^*}\left(P_j^*-\frac{1}{2}\sum_k X_{jk}\theta_k+\sum_{l=1}^{m-1}\sum_{k=l+1}^{m}\theta_l\frac{s_i}{s_l}X_{lk}\theta_k-\frac{1}{2}\frac{\theta_j}{\psi_j}\sum_k\psi_k X_{kj}\right)\right]$
simplified Flory	$\left(\frac{\tilde{v}(\tilde{v}^{1/3}-1)}{\tilde{v}^{1/3}-\frac{4}{3}-\tilde{P}\tilde{v}^2(\tilde{v}^{1/3}-\frac{2}{3})}\right)\left(\frac{\psi_j}{n_j}\right)\left[(\tilde{P}\tilde{v}^2+1)\left(1-\frac{T^*P_j^*}{P^*T_j^*}\right)-2+\frac{2}{P^*}\sum_k P_{jk}^*\psi_k\right]$
lattice fluid	$\left(\frac{1}{2\tilde{p}+\tilde{T}(1-\tilde{v}^{-1}-r^{-1})}\right)\left(\frac{\psi_j}{n_j}\right)\left[(\tilde{P}\tilde{v}^2+1)\left(1-\frac{T^*P_j^*}{P^*T_j^*}\right)-1+\frac{\tilde{T}\tilde{v}}{r}\left(\frac{T^*P_j^*}{P^*T_j^*}-\frac{n_i}{(\psi_j\sum_k n_k)}\right)+\frac{1}{P^*}\left(P_j^*-\sum_k\Delta P_{jk}\psi_k+\frac{1}{2}\sum_l\sum_k\psi_l\Delta P_{lk}^*\psi_k\right)\right]$

[a] See footnotes to Table I.

Table V
Characteristic Equation-of-State Parameters

model and component	v_{sp}^*, cm³/g	P^*, MJ/m³	T*, K
Flory and simplified Flory[a]			
benzene	0.890	577	4780
cyclohexane	1.02	513	5060
polystyrene	0.817	534	7970
lattice fluid[b]			
benzene	1.006	444	523
cyclohexane	1.109	383	497
polystyrene	0.905	357	735

[a] From ref 28. [b] From ref 30.

Then, for each solution theory, the binary benzene–cyclohexane interaction parameter was determined with VLE literature data[33] and the parameter estimation procedure of Ruff et al.[34] by selecting the parameter that minimized the differences between calculated and experimental activity values in the least-squares sense. The solution theory equations provided excellent representations of the benzene–cyclohexane VLE. With this parameter, derivative values (actually $n_3(\partial \ln a_i/\partial n_3)_{T,P,n_1}$) were calculated at each composition using the equations in Tables I through IV and compared with the Redlich–Kister values and with the other polymer solution theory values. The calculations confirmed the solution theory derivative equations.

As an additional comparison, the Flory theory composition derivative of the activity for a binary system has been given by Rostami and Walsh[35] except that the derivative is taken with respect to segment fraction instead of moles, i.e., $(\partial \ln a_1/\partial\psi_2)_{T,P}$. Writing the binary derivative equation from Tables III and IV for the Flory theory and multiplying by $[(\partial\psi_2/\partial n_2)_{T,P,n_1}]^{-1}$ to convert to the segment fraction derivative do, in fact, give their result. Rostami and Walsh further divided the interaction parameter into enthalpic and entropic portions, $X_{12} = X_{12}' + T\tilde{v}Q_{12}$, following the work of Eichinger and Flory.[36]

Characteristic Parameters. Each solution theory requires three pure component characteristic equation-of-state parameters for each component. These parameters are assumed to be independent of temperature, pressure, and composition. The values of the characteristic temperature, pressure, and specific volume were obtained from the literature[28,30] and are presented in Table V.

Segment–Surface Ratios. The Flory theory requires one additional parameter for each component pair, the segment–surface ratio. For comparison, the required ratios were estimated in three different ways: geometric considerations,[37,19] group contribution format,[38] and optimization of the ternary data. For geometric considerations, each solvent molecule was assumed to be a sphere with a volume equal to its close-packed volume per molecule. The polymer was considered to be a cylinder with a mer volume equal to the close-packed volume per repeat unit. The repeating length for polystyrene was taken as 2.5×10^{-8} cm/(repeat unit) (C_8H_8).[37] The optimization of the segment–surface ratios on the experimental data is described in the ternary calculations procedure. The segment–surface ratios obtained from each of the three methods are given in Table VI.

Table VI
Segment–Surface Ratios for the Flory Theory

method	s_1/s_2[a]	s_3/s_2[a]	s_1/s_3[a,b]
geometric considerations[c,d]	2.11	1.98	1.07
group contributions[e]	1.08	1.08	1.00
this work	1.61	1.50	1.07

[a] Notation for benzene (1)–polystyrene (2)–cyclohexane (3). [b] $s_1/s_3 = (s_1/s_2)/(s_3/s_2)$. [c] From ref 37. [d] From ref 19. [e] From ref 38.

Experimental Data. All of the experimental data used were obtained from literature. The benzene (1)–polystyrene (2)–cyclohexane (3) system was used due to the relative abundance of literature data for that system.

The binary solvent–polymer data consisted of the osmotic pressure second virial coefficient of the solvent. Binary data were obtained for systems of various polymer molecular weights and temperatures. Table VII contains the binary data that were used. The data were from light scattering, osmotic pressure, and sedimentation equilibrium experiments.

The ternary solvent–polymer–solvent data consisted of the osmotic pressure second virial coefficient of the solvent mixture and the preferential adsorption coefficient of the polymer. The coefficients were reported at various solvent mixtures while at infinite dilution of the polymer. Tables VIII and IX contain ternary data that are representative of the literature data available. These ternary data, from light scattering and sedimentation equilibrium experiments, were for systems of five polymer molecular weights and two temperatures. These were sets of data that had experimental values for both the preferential adsorption and second virial coefficients.

Table VII
Experimental Binary Solvent–Polymer Data

temp, K	polym mol wt	$A_2 \times 10^5$ cm^3/g^2	ref
	Cyclohexane as Solvent		
293	35 600	−38.0	14
293	117 000	−24.0	14
303	50 500	−2.76	43
313	50 500	6.30	43
323	50 500	13.3	43
303	125 000	−2.45	43
313	125 000	5.78	43
323	125 000	11.3	43
303	359 000	−1.98	43
313	359 000	5.28	43
323	359 000	10.0	43
303	566 000	−1.78	43
313	566 000	5.25	43
323	566 000	9.22	43
308	4 000 000	0.00	44
318	4 000 000	6.40	44
328	4 000 000	8.80	44
296	68 700	−16.7	45
298	68 700	−12.2	45
303	68 700	−5.48	45
308	68 700	0.00	45
313	68 700	4.66	45
318	68 700	8.54	45
305	406 000	−3.23	46
307	406 000	−1.13	46
309	406 000	1.11	46
313	406 000	3.52	46
316	406 000	5.69	46
	Benzene as Solvent		
293	35 600	68.3	14
293	117 000	53.0	14
293	372 000	36.8	14
295	413 000	41.0	47
295	540 000	36.0	47

Table VIII
Experimental Preferential Adsorption Data

benzene vol fractn	λ, cm^3/g				
	set 1[a,b]	set 2[a,c]	set 3[a,d]	set 4[e,f]	set 5[e,g]
0.0	−0.010	−0.027	0.020	0.013	0.031
0.8	0.001	−0.010	0.018		
0.75				0.060	0.049
0.65	0.013	0.019	0.038	0.088	0.077
0.58	0.072	0.041	0.082		
0.5	0.148	0.159	0.126	0.138	0.127
0.4	0.180	0.151	0.189		
0.35				0.151	0.149
0.3	0.114	0.105	0.123		
0.25				0.113	0.115
0.2	0.065	0.079	0.075		
0.1	0.043	0.036	0.041		

[a] From sedimentation equilibrium. [b] From ref 14, T = 293 K, polymer molecular weight, 35 600. [c] From ref 14, T = 293 K, polymer molecular weight, 117 000. [d] From ref 14, T = 293 K, polymer molecular weight, 372 000. [e] From light scattering. [f] From ref 47, T = 295 K, polymer molecular weight, 413 000. [g] From ref 47, T = 295 K, polymer molecular weight, 540 000.

Binary Solvent–Polymer Calculations. The evaluation of the solution theory solvent–polymer interaction parameters at infinite dilution of the polymer was a direct calculation. For each value of A_2 at fixed temperature, pressure, and composition, eq 2 when combined with the solution theory expression for activity is quadratic with respect to the solvent–polymer interaction parameter. Only one of the two roots is physically reasonable, however.

Ternary Solvent (1)–Polymer (2)–Solvent (3) Calculations. With the polymer–solvent interaction parameters obtained from the binary data, two approaches are possible for ternary calculations. The first is to use values for the solvent–solvent interaction parameter obtained from VLE data. Then preferential adsorption values can be calculated for comparison with the actual ternary data. An alternative approach is to use the ternary data to estimate the solvent–solvent parameter. We used both approaches in this work.

Table IX
Experimental Ternary Osmotic Pressure Second Virial Coefficient Data

benzene vol fract	$A_2 \times 10^4$, cm^3 mol/g^2				
	set 1[a,b]	set 2[a,c]	set 3[a,d]	set 4[e,f]	set 5[e,g]
1.0	6.83	5.30	3.68	4.10	3.60
0.9	6.34	5.16	3.72	3.88	3.59
0.8	5.36	5.22	3.54		
0.75				3.89	2.92
0.65	4.68	3.48	3.22	3.69	3.20
0.58	4.29	5.35	3.19		
0.5	4.46	4.31	2.87	3.73	2.85
0.4	3.21	3.48	2.60		
0.35				3.19	2.70
0.3	1.91	2.73	2.02		
0.25				1.48	1.48
0.2	0.0	1.56	1.50		
0.1	−2.30	0.54	0.23		
0.0	−3.80	−2.40			

[a] From sedimentation equilibrium. [b] From ref 14, T = 293 K, polymer molecular weight, 35 000. [c] From ref 14, T = 293 K, polymer molecular weight, 117 000. [d] From ref 14, T = 293 K, polymer molecular weight, 372 000. [e] From light scattering. [f] From ref 47, T = 295 K, polymer molecular weight, 413 000. [g] From ref 47, T = 295 K, polymer molecular weight, 540 000.

For the first approach, the solvent–solvent interaction parameters obtained from the binary VLE data at 298 K were used as the solvent–solvent interaction parameters for the ternary system at 293 K. The VLE data gave the interaction parameters using a data reduction computer program developed by Ruff.[39]

For the second approach, the optimum solvent–solvent interaction parameter was found by minimizing the objective function

$$J = \sum_{i=1}^{m} \left[\left(\frac{\epsilon_\lambda}{\sigma_\lambda^2} \right) (\lambda_i - \hat{\lambda}_i)^2 + \left(\frac{\epsilon_{A_2}}{\sigma_{A_{2,M}}^2} \right) (A_{2,M,i} - \hat{A}_{2,M,i})^2 \right] \quad (10)$$

where m is the number of data points, σ_λ^2 and $\sigma_{A_{2,M}}^2$ are the variances of the experimental data points, and the circumflex denotes a calculated value. The coefficients ϵ_λ and ϵ_{A_2} have values of unity or zero depending on which data (λ or $A_{2,M}$, or both) are chosen for the optimization. The objective function was minimized by forcing the derivative $\partial J/\partial \kappa_{13}$, calculated numerically, to zero.

The confidence interval for the estimate of κ_{13} is calculated by the linearization or Taylor series method for nonlinear parameter estimation.[40] For a 100-γ% confidence interval, the lower and upper bounds of the parameter are given by

$$\kappa_{13} \mp t_{(\nu,(1+\gamma)/2)} \left[\frac{J}{(\beta m - 1)} (\boldsymbol{X}^T \boldsymbol{X})^{-1} \right]^{1/2} \quad (11)$$

where

$$\boldsymbol{X}^T \boldsymbol{X} = \sum_{i=1}^{m} \left[\left(\frac{\epsilon_\lambda}{\sigma_\lambda^2} \right) \left(\frac{\partial \hat{\lambda}_i}{\partial \kappa_{13}} \right)^2 + \left(\frac{\epsilon_{A_2}}{\sigma_{A_{2,M}}^2} \right) \left(\frac{\partial \hat{A}_{2,M,i}}{\partial \kappa_{13}} \right)^2 \right] \quad (12)$$

The variances serve as weight factors in this weighted

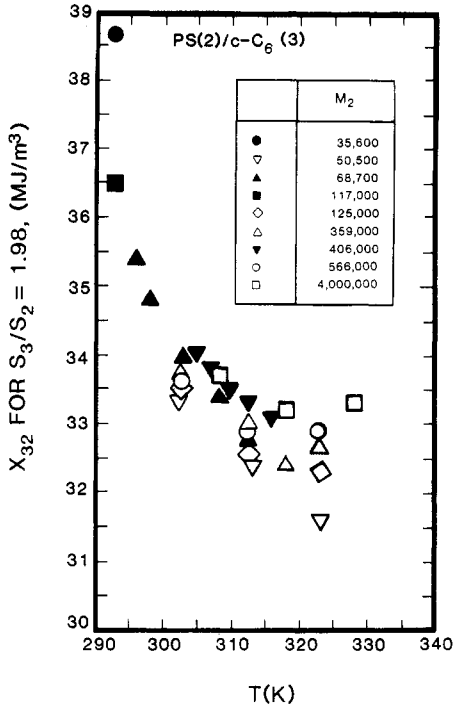

Figure 1. Cyclohexane (3)–polystyrene (2) Flory interaction parameters, $s_3/s_2 = 1.98$.

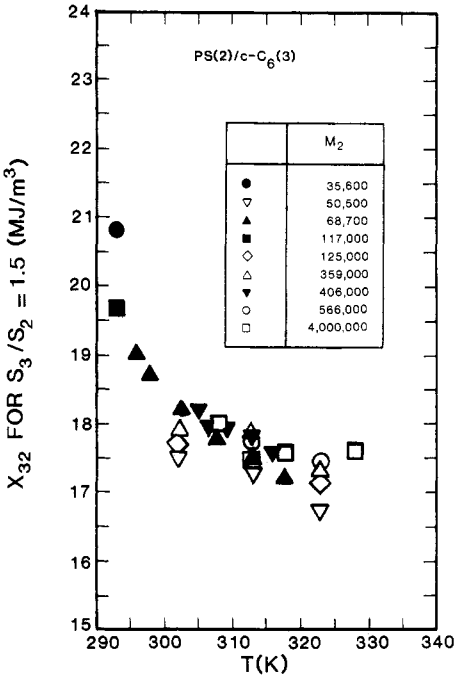

Figure 2. Cyclohexane (3)–polystyrene (2) Flory interaction parameters, $s_3/s_2 = 1.5$.

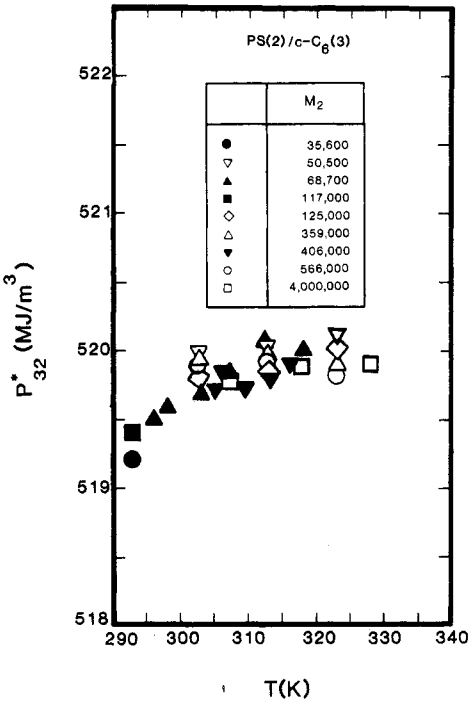

Figure 3. Cyclohexane (3)–polystyrene (2) simplified Flory interaction parameters.

least-squares formulation. In this work, the derivatives in eq 12 were estimated numerically and a 95% confidence interval was used for all calculations.

For the Flory theory, segment–surface ratios could be estimated from group contributions or geometric considerations, as described above, or they can be treated as adjustable parameters and estimated from the ternary data, following the parameter estimation procedure of this section. Again, we followed both approaches. For the parameter estimation procedure, the solvent–solvent segment–surface ratio was set at 1.07. This value, from geometric considerations, provided a better fit to the VLE data than the value from the group contribution format, 0.994. With one segment–surface ratio fixed, selecting one solvent–polymer segment–surface ratio fixed the remaining ratio. The solvent–polymer segment–surface ratios were allowed to vary until an optimum fit was achieved; i.e., the objective function was minimized. Since the polymer–solvent interaction parameters were dependent on the segment–surface ratios, new values of the interaction parameters were calculated each time the ratios changed. The optimum solvent–polymer segment–surface ratios obtained from this method were $s_1/s_2 = 1.61$ and $s_3/s_2 = 1.50$. As shown in Table VI, the optimized segment–surface ratios were essentially an average of those estimated from geometric considerations and those from the group contribution format. Subsequent calculations for these values of segment–surface ratios gave new optimum estimates of the solvent–solvent parameter.

All of the ternary calculations were based on the data of Chu and Munk[14] for the benzene (1)–polystyrene (2)–cyclohexane (3) system at 293 K and a single polymer molecular weight of 117 000. Data at these conditions appear to be typical, and optimizations that include the other sets of data do not change the essence of our conclusions. The polymer was assumed to be at infinite dilution in the solvent mixture.

Results and Discussion

Binary Solvent–Polymer. The results from the cyclohexane (3)–polystyrene (2) interaction parameter evaluations for the several theories are shown in Figures 1–4. For the Flory theory, two sets of results are given depending on whether the segment–surface ratios were obtained from geometric considerations (Figure 1) or by optimizing calculations to the ternary data (Figure 2). Segment–surface ratios calculated with the group contribution format for these binary systems are close to unity, the value for which the Flory theory corresponds to the simplified Flory theory. Consequently, no results are shown for this method of calculating segment–surface ratios. The results for the benzene (1)–polystyrene (2) system for the several theories are given in Table X. The dependence of the interaction parameters on the polymer molecular weight mirrors the variation of A_2 and generally

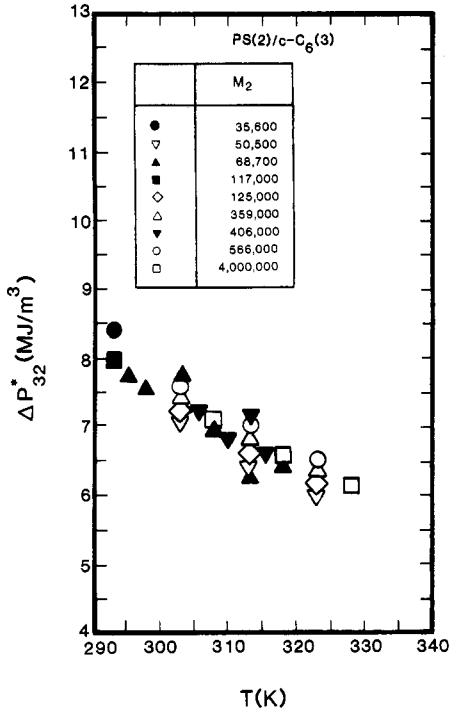

Figure 4. Cyclohexane (3)–polystyrene (2) lattice fluid interaction parameters.

Table X
Benzene (1)–Polystyrene (2) Interaction Parameters

		interaction parameter, MJ/m³			
T, K	polym mol wt	Flory s_1/s_2 = 2.11	Flory s_1/s_2 = 1.62	simplified Flory	lattice fluid
293	35 600	37.3	20.1	551.7	10.7
293	117 000	41.0	22.2	551.3	11.2
293	372 000	44.6	24.1	551.0	11.8
295	413 000	44.0	23.8	551.1	11.7
295	540 000	45.1	24.4	551.0	11.9

is consistent with the excluded volume theory.

For the Flory and simplified Flory theories, parameter values for the benzene–polystyrene and cyclohexane–polystyrene systems are available in the literature and generally are consistent with our values. For the Flory cyclohexane (3)–polystyrene (2) interaction parameter, X_{32}, Höcker, Shih, and Flory[41] report values of the enthalpic and entropic contributions[36] at 298 K, using a solvent–polymer segment–surface ratio of 2.0, and for a polymer molecular weight of 51 000. Their results were reported for the entire concentration range. From these results we calculate a value of X_{32} of 33.2 MJ/m³ at 298 K. This compares well with a value of 33.8 MJ/m³ obtained by extrapolating values of 303, 313, and 323 K to 298 K for a molecular weight of 50 500 (Figure 1), as well as a value of 34.8 MJ/m³ at 298 K (Figure 1) for a molecular weight of 68 700.

For the simplified Flory theory, values for both the cyclohexane (3)–polystyrene (2) and benzene (1)–polystyrene (2) interaction parameters were available in the literature for the polymer-rich region.[28] For the cyclohexane (3)–polystyrene (2) system at 297, 307, and 317 K, the interaction parameters reported ranged from 509.7 to 510.3 MJ/m³. The values from Figure 3 vary from 519.6 to 520.0 MJ/m³ for the same temperature range. The value for the benzene (1)–polystyrene (2) interaction parameter was 552.6 MJ/m³ at 293 K. From Table X, the interaction parameters at 293 K from this work were 551.7, 551.3, and 551.0 MJ/m³, depending on molecular weight. The discrepancy for the cyclohexane–polystyrene system is significant and may indicate a dependence of this parameter on concentration for this system. The benzene–polystyrene parameters are in excellent agreement.

Table XI
Cyclohexane (1)–Polybutadiene (2) Interaction Parameters

	interaction parameter,[a] MJ/m³		
T, K	Flory s_1/s_2 = 0.93	simplified Flory	lattice fluid
302[b]	14.1	592.8	8.2
333[c]	18.6	591.0	5.9
355[c]	19.3	590.9	4.1
373[c]	20.2	590.6	3.2

[a] Solvent (1)–polymer (2) interaction parameter. [b] This work, using the data of ref 42. [c] Gas chromatography results, ref 31.

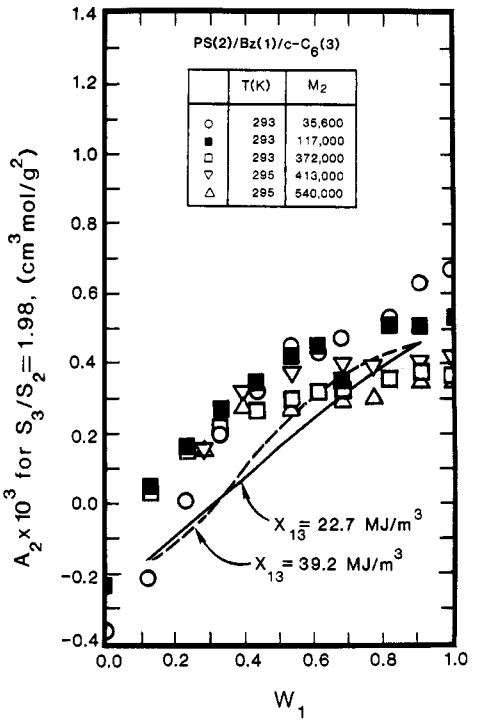

Figure 5. Flory model ternary osmotic pressure second virial coefficient s_1/s_2 = 2.11, s_3/s_2 = 1.98.

Comparisons of the parameters to literature values could be made for all three solution theories using the cyclohexane–polybutadiene system. For a polymer molecular weight of 250 000 at a temperature of 301.8 K, the osmotic pressure second virial coefficient for this system has been reported to be 9.77×10^{-4} cm³ mol/g².[42] With this value and for each theory applied to eq 2, the parameters obtained in this work compared favorably with parameters for the polymer-rich region, determined with perturbation gas chromatography data[31] (Table XI).

Ternary Solvent (1)–Polymer (2)–Solvent (3). The ternary system results, based on an â priori solvent–solvent parameter determined from benzene–cyclohexane VLE as well as those based on optimizations of the solvent–solvent interaction parameters to the ternary mixture second virial or preferential adsorption coefficient data, are shown in Figures 5–14. The values of the polymer–solvent parameters used in these ternary calculations were held fixed at the values obtained from binary calculations and are summarized in Table XII. Figures 5–8 illustrate the results when only the second virial coefficient data were used to estimate the solvent–solvent parameter. Figures 9–12 illustrate the results when only the preferential adsorption coefficient data were used. Table XIII gives the standard deviations characterizing the agreement between the

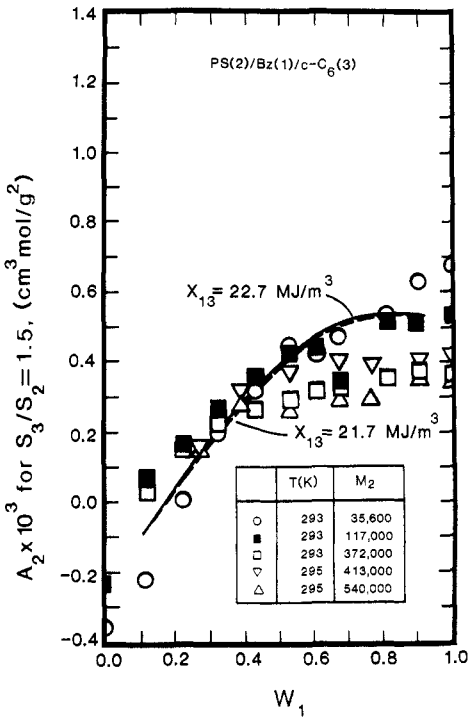

Figure 6. Flory model, ternary osmotic pressure second virial coefficient $s_1/s_2 = 1.61$, $s_3/s_2 = 1.50$.

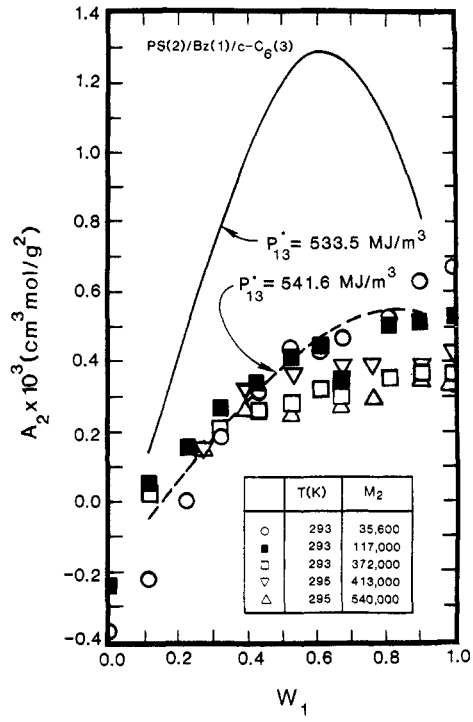

Figure 7. Simplified Flory model, ternary osmotic pressure second virial coefficient.

Table XII
Solvent-Polymer Interaction Parameters Used in Ternary Models

model	κ_{32},[a] MJ/m^3	κ_{12},[a] MJ/m^3
Flory ($s_1/s_2 = 2.11$, $s_3/s_2 = 1.98$)[b]	41.0	36.5
Flory ($s_1/s_2 = 1.61$, $s_3/s_2 = 1.5$)[c]	22.2	19.7
simplified Flory	551.3	519.3
lattice fluid	11.2	8.0

[a] κ_{ij} represents the solvent–polymer interaction parameter for the benzene (1)–polystyrene (2)–cyclohexane (3) system at 293 K and a polymer molecular weight of 117 000. [b] Surface–segment ratios from geometric considerations. [c] Surface–segment ratios from optimization on ternary data.

Table XIII
Ternary Model Standard Deviations and Optimized Solvent-Solvent Interaction Parameters

	$A_{2,M}$		λ	
model	κ_{13},[a] MJ/m^3	std dev, cm^3 mol/g^2	κ_{13},[a] MJ/m^3	std dev, cm^3/g
Flory (s_1/s_2 =	22.7[b]	2.0×10^{-4}	22.7[b]	6.5×10^{-2}
2.11, s_3/s_2 =	39 ± 67[c,d]	1.8×10^{-4}	52 ± 15[c,d]	4.9×10^{-2}
1.98	44 ± 35[d,e]	1.8×10^{-4}	44 ± 35[d,e]	5.1×10^{-2}
Flory (s_1/s_2 =	22.7[b]	9.5×10^{-5}	22.7[b]	6.2×10^{-2}
1.61, s_3/s_2 =	22 ± 8[c,d]	9.4×10^{-5}	40 ± 19[c,d]	5.4×10^{-2}
1.5)	24 ± 5[d,e]	9.6×10^{-5}	24 ± 5[d,e]	6.1×10^{-2}
simplified	533.5[b]	6.6×10^{-4}	533.5[b]	5.2×10^{-2}
Flory	511.7 ± 0.8[c,d]	8.3×10^{-5}	532 ± 8[c,d]	5.2×10^{-2}
	541.5 ± 0.6[d,e]	8.4×10^{-5}	541.5 ± 0.6[d,e]	6.7×10^{-2}
lattice fluid	17.2[b]	7.5×10^{-4}	17.2[b]	5.2×10^{-2}
	3 ± 1[c,d]	8.7×10^{-5}	20 ± 12[c,d]	5.1×10^{-2}
	3 ± 1[d,e]	8.7×10^{-5}	3 ± 1[d,e]	6.9×10^{-2}

[a] κ represents the benzene (1)–cyclohexane (3) interaction parameter. [b] From binary solvent VLE data. [c] Optimized on $A_{2,M}$ data. [d] 95% confidence interval. [e] Optimized on both $A_{2,M}$ and λ data.

calculated and experimental values for all cases, as well as the optimum solvent–solvent interaction parameters and their confidence intervals.

Second Virial Coefficients. The results in Figures 5–8 (dashed lines) show that all of the theories considered were

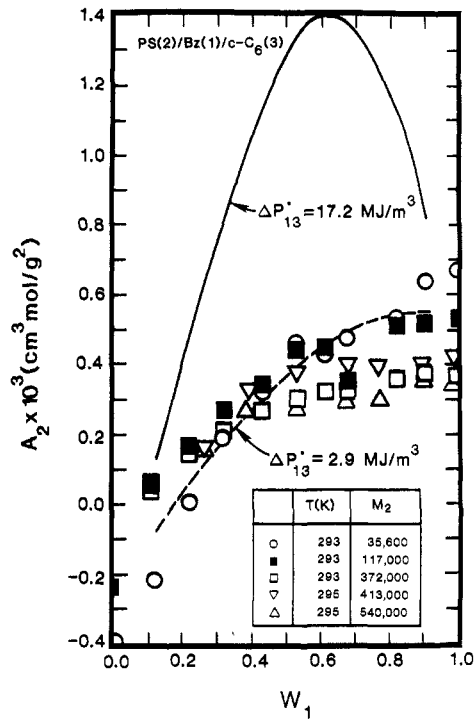

Figure 8. Lattice fluid model, ternary osmotic pressure second virial coefficient.

capable of modeling the $A_{2,M}$ values when the solvent–solvent binary interaction parameter was suitably adjusted. For the simplified Flory and lattice fluid models, this required significant adjustment away from the value obtained from the benzene–cyclohexane VLE data. Using the VLE parameters without adjustment predicts considerable enhanced mixed-solvent power near a benzene weight fraction of 0.6 (solid lines, Figures 7 and 8), contrary to the reported experimental results. For the Flory model, a reasonable, if not optimum, fit could be obtained with a priori estimates of both segment–surface ratios (at least

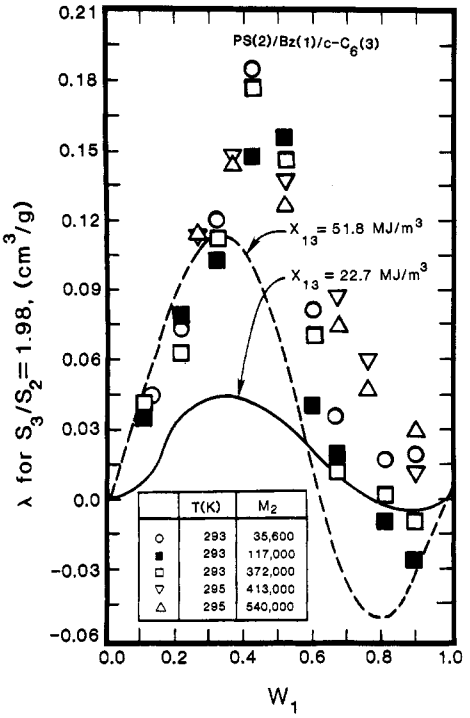

Figure 9. Flory model, preferential adsorption coefficient, $s_1/s_2 = 2.11$, $s_3/s_2 = 1.98$.

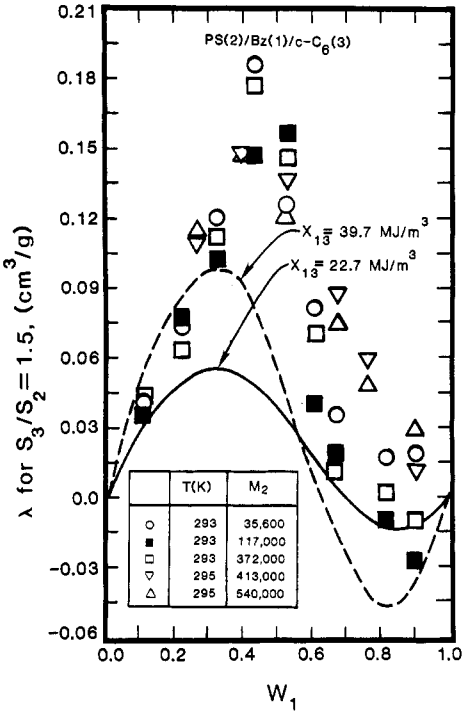

Figure 10. Flory model, preferential adsorption coefficient, $s_1/s_2 = 1.61$, $s_3/s_3 = 1.50$.

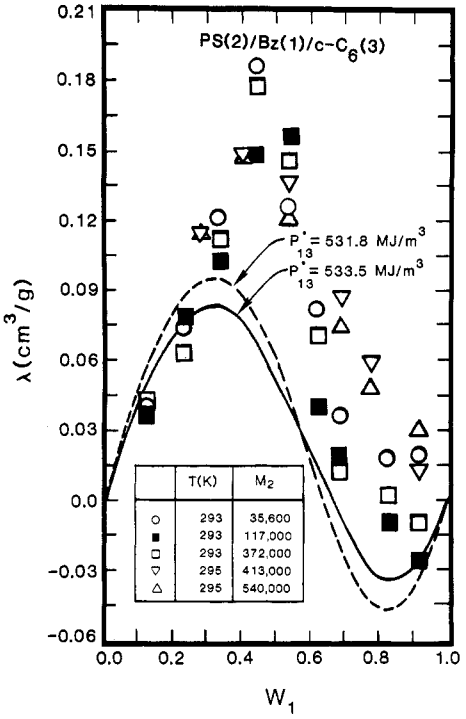

Figure 11. Simplified Flory model, preferential adsorption coefficient.

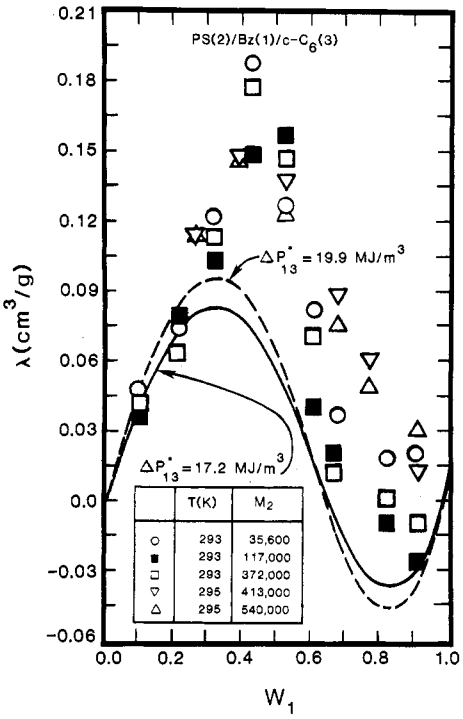

Figure 12. Lattice fluid model, preferential adsorption coefficient.

if calculated from geometric considerations) and the benzene–cyclohexane interaction parameter (based on binary VLE) (solid line, Figure 5). This fit was improved considerably by adjusting the segment–surface ratios and then readjusting the binary solvent–solvent parameter (solid line, Figure 6). The amount of this latter readjustment required for an optimum fit was minimal, and the parameter remained essentially at the VLE value. On the basis of the predictive capability with these data, the Flory model clearly is the better choice. In fact, using an average of the geometric and Bondi segment–surface ratios and the benzene–cyclohexane VLE interaction parameter does as well as the fitted model.

The effect of changing the Flory segment–surface ratios while holding the solvent–solvent binary interaction parameter constant at the VLE value can be seen in Figures 5–7 (solid lines). Figure 7, equivalent to Flory model calculations using segment–surface values of unity, shows a distinct maximum in solvent power. Using solvent/polymer segment–surface ratios near 2 gives a nearly linear variation between the two pures (Figure 5) and using an approximate average of these two cases gave the solid curve in Figure 6. The segment–surface ratio is a significant parameter, having considerable effect on the calculated behavior. These conclusions are consistent with those

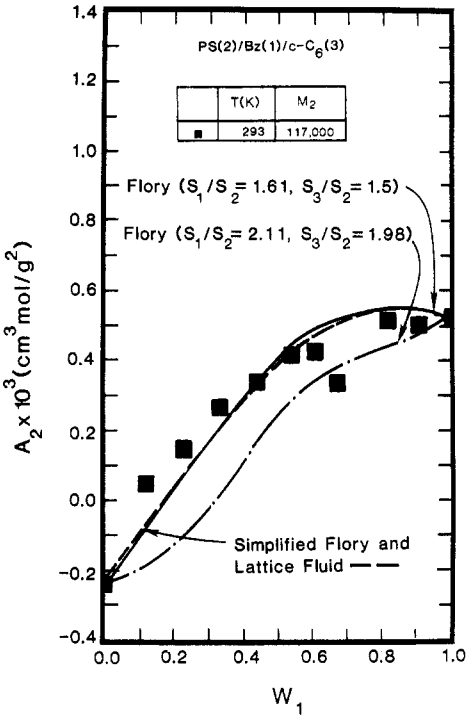

Figure 13. Ternary models, osmotic pressure second virial coefficient, full optimization.

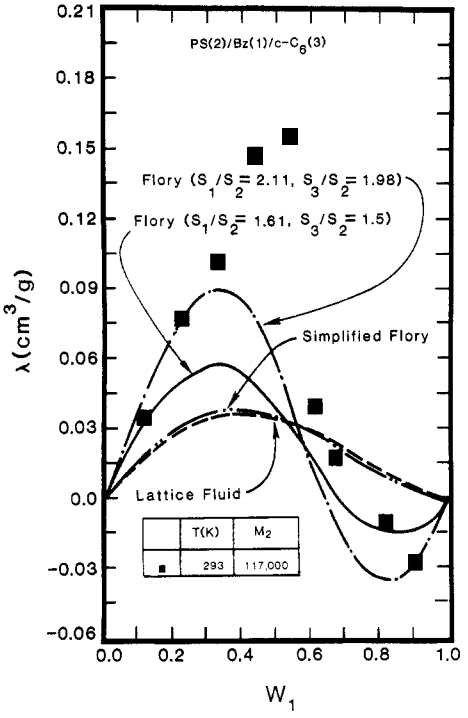

Figure 14. Ternary models, preferential adsorption coefficient, full optimization.

reported previously,[20,21] in which significant effects of s were also observed and comparable adjustments were required in the geometric-based segment–surface ratios.

Figures 7 and 8 indicate that the simplified Flory and lattice fluid models behave very similarly in these calculations. Using the VLE-determined solvent–solvent binary interaction parameter resulted in similar second virial coefficient curves, and the optimum curve fits are essentially the same. The lattice fluid model, which accounts for surface contact dissimilarity in an implicit manner, is no more effective than the simplified Flory model, which eliminates the effect altogether.

Preferential Adsorption Coefficients. Preferential adsorption coefficient calculations are shown in Figures 9–12, where it is seen that all of the models had considerably more difficulty with these data than with the second virial coefficient. The models were unable to reproduce the maximum in λ near a benzene weight fraction of 0.5 without going significantly negative at a weight fraction of 0.8. Although the negative peak is smaller than the positive, it still is a significant deviation from the experimental results. Consequently, λ is underestimated by the models for the bulk of the weight fraction range in each case. The curves with a more positive maximum are, strictly speaking, better representations of the data, although the improvement is not dramatic due to larger error caused by the deeper minimum and as indicated by the standard deviations (Table XIII).

With the VLE solvent–solvent parameters (solid lines), the simplified Flory and lattice fluid models did the best at predicting λ. Only marginal improvement was gained by further adjusting this parameter. The full Flory model, starting with poorer predictions, showed improvement, upon adjusting the solvent–solvent parameter, to about the same level as the optimized simplified Flory and lattice fluid models.

The preferential adsorption coefficient results, like the second virial coefficient calculations, show that the simplified Flory and lattice fluid models behave very similarly, at least for this system. The calculations for the two models using the VLE solvent–solvent parameter were virtually identical, as were those using the optimally adjusted parameter.

Combined Optimizations. Figures 13 and 14 show the ability of the models to represent both $A_{2,M}$ and λ using the same parameters. Because adjusting the solvent–solvent parameter produces only marginal improvement in estimating λ, optimizing on both $A_{2,M}$ and λ produces essentially the same result as when $A_{2,M}$ alone is used. In terms of á priori predictions, the Flory model is the most successful. Even using geometric segment–surface ratios and the VLE-determined solvent–solvent interaction parameter produced reasonable representations of both sets of data. Using a value for the segment–surface ratio intermediate between the geometric and group contribution values did very well for the second virial coefficient and slightly better for λ.

Conclusion

Equations obtained for relating species activities to A_2 and λ can be used in conjunction with experimental data to estimate parameters in polymer solution theories. Binary solvent–polymer systems yield solvent–polymer interaction parameters and ternary solvent–polymer–solvent systems yield solvent–solvent parameters and (for the Flory theory) segment–surface ratios.

The segment–surface ratio of Flory was found to be a significant factor in establishing the dependence of both $A_{2,M}$ and λ on the solvent mixture composition for the system studied. Consequently, a simplification of the Flory theory that eliminates this effect is not recommended. Even the lattice fluid theory, which allows for this effect indirectly, appears to behave as though the ratios are largely ignored.

Although the Flory theory gave the best overall á priori predictions for the benzene–polystyrene–cyclohexane system, it still showed some significant short-comings in predicting λ. Further study of this result is needed.

Finally, data and calculations on several systems suggest that the binary solvent–polymer parameters for these theories may be nearly concentration independent. Values

determined for the polymer-rich region using gas chromatography are consistent with those determined at infinite dilution in polymer using light scattering, osmotic pressure, or sedimentation equilibrium.

Notation

A_2	osmotic pressure second virial coefficient of the solvent in a solvent–polymer system
$A_{2,M}$	osmotic pressure second virial coefficient of the solvent mixture in a solvent–polymer–solvent system
a_i	activity of component i in solution
C	polymer concentration (mass/volume)
J	objective function for solvent–solvent interaction parameter evaluation
M_i	mass average molecular mass of component i
m	number of species in solution (polymer solution theories) or number of data points used for estimating solvent-solvent parameter (eq 10–12)
n	refractive index
n_i	moles of component i
P	absolute pressure
$\tilde{P}$	mixture reduced pressure, $\tilde{P} = P/P^*$
P^*	characteristic pressure for a mixture
P_{ij}^*	lattice fluid interaction parameter
ΔP_{ij}^*	simplified Flory interaction parameter
$\tilde{P}_i$	reduced pressure for component i, $\tilde{P}_i = P/P_i^*$
P_i^*	characteristic pressure of component i
R	gas constant
r	number of segments per mole for the mixture
r_i	number of segments per mole for species i
r_i°	number of segments per mole for species i in the pure state
s_i	number of intermolecular contact sites per segment
T	absolute temperature
$\tilde{T}$	mixture reduced temperature, $\tilde{T} = T/T^*$
$\tilde{T}_i$	reduced temperature for species i, $\tilde{T}_i = T/T_i^*$
T^*	characteristic temperature for the mixture, defined by the mixing rules in Table II
T_i^*	characteristic temperature for species i
$t_{(\nu,(1+\gamma)/2)}$	cummulative t distribution of statistics
$\tilde{v}$	mixture reduced volume
v^*	mixture characteristic volume per segment
v_i	volume per segment for species i
$\tilde{v}_i$	reduced volume for species i, v_i/v_i^*
v_i^*	characteristic volume per segment for species i
v_{isp}^*	characteristic close-packed volume per unit mass for species i
X_{ij}	Flory interaction parameter

Subscripts

1	solvent (1)
2	polymer (2)
3	solvent (3)

Greek Letters

β	1 if $A_{2,M}$ data only or λ data only are used to estimate κ_{13}; 2 if both $A_{2,M}$ and λ data are used
γ	confidence interval for parameter estimates, $0 < \gamma < 1$
δ_{ij}	kronecker delta, $\delta_{ij} = 0$ for $i \neq j$; $\delta_{ij} = 1$ for $i = j$
ϵ_λ	objective function coefficient; unity if preferential adsorption coefficient data were used, zero if not
$\epsilon_{A_{2,M}}$	objective function coefficient; unity if osmotic pressure second virial coefficient data were used, zero if not
θ_i	site fraction of species i, $\theta_i = r_i n_i s_i/(\sum r_j n_j s_j)$
κ	represents a binary interaction parameter
λ	preferential adsorption coefficient of the polymer
μ_i	chemical potential of species i
ν	number of degrees of freedom in estimating κ_{13} ($=\beta m - 1$)
$\tilde{\rho}$	reduced density for the mixture, $=1/\tilde{v}$
$\tilde{\rho}_i$	reduced density of species i $=1/\tilde{v}_i$
σ_λ^2	variance of experimental preferential adsorption coefficients
$\sigma_{A_{2,M}}^2$	variance of the experimental osmotic pressure second virial coefficients
ϕ_i	volume fraction before mixing for the polymer-free solvent mixture
χ	Flory–Huggins binary interaction parameter
ψ_i	segment fraction of species i, $\psi_i = r_i n_i/(\sum r_j n_j)$
ψ_i°	pure state segment fraction of species i, $\psi_i^\circ = r_i^\circ n_i/(\sum r_j^\circ n_j)$

Registry No. Cyclohexane, 110-82-7; polystyrene, 9003-53-6; benzene, 71-43-2; polybutadiene, 9003-17-2.

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Probe Diffusion in Solutions of Long-Chain Polyelectrolytes†

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ABSTRACT: Light-scattering spectroscopy was used to measure the diffusion of polystyrene latex spheres through solutions of partially neutralized poly(acrylic acid), as a function of polymer concentration, pH, ionic strength, and probe radius. D/D_0 follows a stretched exponential form $\sim\exp(-ac^{\nu}I^{\beta}R^{\delta})$, with $\nu \simeq 0.5$–1 (depending on I), $\beta \simeq -0.8$, and $\delta \simeq 0.2$, the last of these being substantially inconsistent with most theoretical models for probe diffusion. With partially (>50%) neutralized polymer, small (400 Å) probe particles diffuse much (up to eightfold) faster than predicted by the Stokes–Einstein equation; the validity of the Stokes–Einstein equation improves at higher ionic strength and for larger (up to 1.3 μm) probe particles.

Introduction

The diffusion of globular probe particles through polymer solutions is a phenomenon of considerable scientific and practical interest. The probe diffusion coefficient gives valuable information, different from that elsewise available, on polymer dynamics. Probe diffusion is a model for such scientific phenomena as inter- and intracellular transport in living tissues. Particle motion in polymer solutions may also occur during a variety of potentially practical circumstances, such as the production of long-chain polysaccharides by bacterial fermentation or the electrophoretic preparation of whole cells by free (unsupported) Tiselius electrophoresis.

We have previously reported studies on the diffusion of weakly charged probes (polystyrene latex spheres, serum albumin molecules) through aqueous solutions of poly(ethylene oxide),[1-3] poly(acrylic acid),[4-6] and bovine serum albumin.[7] In these systems, electrostatic forces between probe and polymer were relatively small: the polyacrylic acids studied by Lin and Phillies[4-6] were not neutralized. Since carboxylic acid groups are weak acids, in their work each polymer chain would have contained only a few ionized carboxylate groups. The serum albumin studies were all performed in 0.15 or 0.5 M NaCl, so electrostatic interactions in the serum albumin solutions were substantially screened.

In our previous work,[1-8] D usually followed a "stretched exponential" form

$$D/D_0 = \exp[-ac^{\nu}M^{\gamma}R^{\delta}] \quad (1)$$

where D_0 is the probe diffusion coefficient in pure solvent, c and M are the polymer concentration and molecular weight, and R is the probe radius. a, ν, γ, and δ are fitting parameters. Stretched exponential forms also describe the macroscopic viscosity η of our polymer solutions. Furthermore, one of us[9] has recently shown that the entirety of the published modern data on polymer and biopolymer self-diffusion in solution is accurately described by stretched exponential forms. We were therefore motivated to apply generalizations of eq 1 to the results described below.

The Stokes–Einstein equation has long been used to interpret the diffusion coefficients of spherical bodies in simple liquids, the usually-assumed condition for the validity of the Stokes–Einstein equation being that the probe radius R is much larger than the radius of any of the surrounding solvent molecules. Surprisingly, even with very large (R = 1.5 μm) probes, the Stokes–Einstein equation fails in some high-molecular-weight polymer solutions.[1-7]

We define the apparent hydrodynamic radius R_{ap} as

$$R_{ap} = \frac{k_B T}{6\pi\eta D} \quad (2)$$

the hydrodynamic radius R_0 measured in pure solvent by

$$R_0 = \frac{k_B J}{6\pi\eta D_0} \quad (3)$$

and the non-Stokes–Einsteinian interaction parameter as

$$K = R_{ap}/R_0 \quad (4)$$

Here k_B, T, and D_0 are Boltzmann's constant, the absolute temperature, and the diffusion coefficient in pure solvent, respectively. For spherical particles, eq 3 is the Stokes–Einstein equation. The probe radius R of eq 1 is identified with R_0. At large c, one finds[1-7] $K < 1$ (sometimes $K \ll 1$). Such obvious artifacts as polymer binding or probe

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