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Thermodynamic Properties of Polystyrene in Mixed Solvents Studied by Sedimentation Equilibrium

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ABSTRACT: The theory of the osmotic and sedimentation equilibria of polymers in mixed solvents is reviewed and the relations between the free enthalpy of mixing ΔG_{mix} and the second virial coefficient as well as the preferential adsorption of solvent components onto polymer are formulated. The method of sedimentation equilibrium is employed for measurement of the latter quantities. Three samples of polystyrene are measured in two combinations of solvents (benzene–cyclohexane and ethyl acetate–cyclohexane) over the whole range of composition of solvent mixtures. The experimental results are analyzed using a general phenomenological expression for ΔG_{mix}. For a reasonable fit, ternary interaction parameters must be introduced into the expression for ΔG_{mix}.

When a mixture of two liquids is used as a solvent for macromolecules, its solvent power is usually quite different from the averaged solvent power of the two pure solvent components. Such solutions also exhibit preferential adsorption of one solvent onto polymer.

The basic understanding of these phenomena was achieved during the 1950's and the early 1960's.[1-11] During the last decade the interest in polymers in mixed solvents has been surging. A large number of methods have been used for measurement of preferential adsorption: diffusion,[12,13] isopiestic distillation,[14] swelling of gels,[15] and membrane equilibria.[16-22] However, the method of light scattering has been used most frequently.[23-40] Sedimentation equilibrium, which may provide essentially the same information as light scattering, has been employed rather rarely.[26,41-43]

The solvent power of a mixed solvent may be studied through the second virial coefficient, which may be obtained from measurements of osmotic pressure, sedimentation equilibrium, or light scattering.[24,25,27] However, the experimentally less demanding measurement of intrinsic viscosity is routinely used for this purpose.[17,29,30,34,35,39,44-50]

Accumulating experimental evidence pointed to the inadequacy of the early oversimplified treatments. The necessity of building a more sophisticated model of three-component systems has been recognized in a series of papers.[51-56] Several publications[10,25,57,58] conveniently summarize some aspects of all these problems.

Recently, we have developed a powerful evaluation technique of sedimentation equilibriuim experiments[59-61] using automatic scanning of photographic plates[62] and extensive computer analysis. The method is capable of yielding the preferential adsorption coefficient and second virial coefficient in a single experiment. In the present study, the method is applied to three polystyrene samples with narrow distribution of molecular weights dissolved in two combinations of solvents (benzene + cyclohexane; ethyl acetate + cyclohexane). The whole range of compositions of these solvent mixtures is studied.

In our hands, none of the existing theories described the phenomenon in reasonable agreement with experiment. In this study, we first describe the phenomenon and derive the basic formulas. These formulas are then applied to a phenomenological expression for ΔG_{mix}. The resulting relations are then used for the analysis of our experimental data for the second virial coefficient and the preferential adsorption parameter.

Theoretical

In this work, we will use several composition variables: number of moles n_i, concentration c_i (in g/mL), molality m_i, and volume fraction *before mixing* ϕ_i. In our notation, the indices 1, 2 will be used for the two solvent components, index 3 for macromolecules. The subscript μ means constant chemical potential of both solvent components; m_i is the constant molality of the ith component. Superscript zero will be used for designation of the quantity

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in the limit of vanishing polymer concentration. RT and P have their usual meaning; $\bar{V}_j$ and $\bar{v}_j$ denote partial molar and specific volumes of the j component, respectively.

For the three-component system, the concentration scales may be related with each other as

$$m_i = 1000n_i/n_1M_1 \tag{1}$$

$$c_i = m_iM_i/\bar{V}_m \tag{2}$$

$$\phi_i = n_iV_i/V_m \tag{3}$$

$$V_m = n_1V_1 + n_2V_2 + n_3V_3 \tag{4}$$

$$\bar{V}_m = n_1\bar{V}_1 + n_2\bar{V}_2 + n_3\bar{V}_3 \tag{5}$$

$$\rho = (n_1M_1 + n_2M_2 + n_3M_3)/\bar{V}_m \tag{6}$$

Here V_m and $\bar{V}_m$ are the total volume of solutions before mixing and after mixing, respectively. ρ is density; M_i and V_i are respectively the molecular weight and the molar volume before mixing of the ith component.

Preferential Adsorption. The preferential adsorption is most conveniently described in terms of osmotic equilibrium using molality as the concentration unit. Our experimental system, a polymer in a mixed solvent at a given constant temperature, is fully described by three independent variables. It is convenient to choose for them pressure and the molalities m_2 and m_3, component one being considered as the principal solvent. In this notation, the change of the chemical potential μ_i of the two solvent components during any process is expressed as

$$\mathrm{d}\mu_1 = \left(\frac{\partial\mu_1}{\partial m_3}\right)_{m_2,P}\mathrm{d}m_3 + \left(\frac{\partial\mu_1}{\partial m_2}\right)_{m_3,P}\mathrm{d}m_2 + \left(\frac{\partial\mu_1}{\partial P}\right)_{m_2,m_3}\mathrm{d}P \tag{7}$$

$$\mathrm{d}\mu_2 = \left(\frac{\partial\mu_2}{\partial m_3}\right)_{m_2,P}\mathrm{d}m_3 + \left(\frac{\partial\mu_2}{\partial m_2}\right)_{m_3,P}\mathrm{d}m_2 + \left(\frac{\partial\mu_2}{\partial P}\right)_{m_2,m_3}\mathrm{d}P \tag{8}$$

Let us consider the following hypothetical experiment: The composition and pressure on one side of the osmotic chamber are changed while the equilibrium with the unchanged other side is preserved. The basic condition for osmotic equilibrium is that the chemical potential of every diffusible component across the membrane is the same on both sides of the membrane. That implies for our hypothetical experiment that

$$\mathrm{d}\mu_1 = \mathrm{d}\mu_2 = 0 \tag{9}$$

To simplify the calculations, it is convenient to define quantity a_{ij} as

$$a_{ij} \equiv \left(\frac{\partial\mu_i}{\partial m_j}\right)_{P,T,m_{k\neq j}} \tag{10}$$

Under the condition of constant chemical potential of diffusible components (i.e., using eq 9) eq 7 and 8 could be transformed to eq 11 and 12, respectively.

$$a_{13} + a_{12}\left(\frac{\partial m_2}{\partial m_3}\right)_\mu + \bar{V}_1\left(\frac{\partial P}{\partial m_3}\right)_\mu = 0 \tag{11}$$

$$a_{23} + a_{22}\left(\frac{\partial m_2}{\partial m_3}\right)_\mu + \bar{V}_2\left(\frac{\partial P}{\partial m_3}\right)_\mu = 0 \tag{12}$$

Equations 11 and 12 are now solved for $(\partial P/\partial m_3)_\mu$ and $(\partial m_2/\partial m_3)_\mu$.

$$\left(\frac{\partial P}{\partial m_3}\right)_\mu = -\frac{a_{12}a_{23} - a_{22}a_{13}}{a_{12}\bar{V}_2 - a_{22}\bar{V}_1} \tag{13}$$

$$\left(\frac{\partial m_2}{\partial m_3}\right)_\mu = -\frac{a_{13}\bar{V}_2 - a_{23}\bar{V}_1}{a_{12}\bar{V}_2 - a_{22}\bar{V}_1} \tag{14}$$

It is convenient to eliminate a_{12} and a_{13} from the above equations by using the Gibbs–Duhem relation written as

$$\frac{1000}{M_1}a_{12} + m_2a_{22} + m_3a_{23} = 0 \tag{15}$$

$$\frac{1000}{M_1}a_{13} + m_2a_{23} + m_3a_{33} = 0 \tag{16}$$

Using eq 15 and 16 together with eq 5, eq 13 and 14 are transformed to

$$\left(\frac{\partial P}{\partial m_3}\right)_\mu = \frac{m_3(a_{33} - [a_{23}{}^2/a_{22}])}{\bar{V}_m - m_3(\bar{V}_3 - [a_{23}/a_{22}]\bar{V}_2)} \tag{17}$$

$$\left(\frac{\partial m_2}{\partial m_3}\right)_\mu = -\frac{a_{23}}{a_{22}}\,\frac{\bar{V}_\mathrm{m} - m_3(\bar{V}_3 - [a_{33}/a_{23}]\bar{V}_2)}{\bar{V}_\mathrm{m} - m_3(\bar{V}_3 - [a_{23}/a_{22}]\bar{V}_2)} \tag{18}$$

In the limit of vanishing concentration of polymer, eq 18 reads

$$(\partial m_2/\partial m_3)_\mu{}^0 = -(a_{23}/a_{22})^0 \tag{19}$$

The last expression $(\partial m_2/\partial m_3)_\mu{}^0$ represents the amount of solvent component 2 which must be added together with 1 mol of the polymer in our hypothetical osmotic experiment. It is a very convenient measure of preferential adsorption. The quantity $(\partial P/\partial m_3)_\mu$ can be transformed into a form using a more convenient concentration unit c_3 (g/mL) as

$$\left(\frac{\partial P}{\partial c_3}\right)_\mu = \frac{c_3\bar{V}_m(a_{33} - [a_{23}{}^2/a_{22}])}{M_3{}^2[1 - c_3(\bar{v}_3 - \bar{v}_2(M_2/M_3)(a_{23}/a_{22}))]^2} \tag{20}$$

The integration of eq 20 and expansion into series in powers of c_3 yield the second virial coefficient A_2 as

$$A_2 = \left[\frac{m_3(a_{33} - [a_{23}{}^2/a_{22}]) - RT}{2c_3M_3RT}\right]^0 \tag{21}$$

Density Increments of Polymer. As we will see later, the phenomenon of preferential adsorption in the mixed solvent systems is related to the density increments at constant composition of solvent mixtures $(\partial\rho/\partial c_3)_{m_2,P}$ and at constant chemical potential $(\partial\rho/\partial c_3)_\mu$.

The quantity $(\partial\rho/\partial c_3)_{m_2,P}$ at constant composition can be obtained by the manipulation of eq 1–5 and the Gibbs–Duhem relation as

$$\left(\frac{\partial\rho}{\partial c_3}\right)_{m_2,P} = \frac{1 - \bar{v}_3\rho}{1 - c_3\bar{v}_3} \tag{22}$$

This expression is valid even if the molar volumes depend on composition, i.e., if $\Delta V_\mathrm{mix} \neq 0$. In the limit of vanishing polymer concentrations, eq 22 reduces to

$$\lim_{c_3\to 0}\left(\frac{\partial\rho}{\partial c_3}\right)_{m_2,P} \equiv \left(\frac{\partial\rho}{\partial c_3}\right)^0_{m_2,P} = 1 - \bar{v}_3{}^0\rho^0 \tag{23}$$

The standard analysis of the preferential adsorption employs the concept of a density increment at constant chemical potential of both solvents, $(\partial\rho/\partial c_3)_\mu$, i.e., an increment which is related to the liquids which are in osmotic equilibrium. Standard treatment yields

$$\left(\frac{\partial\rho}{\partial m_3}\right)_{\mu} = \left(\frac{\partial\rho}{\partial m_2}\right)_{m_3,P}\left(\frac{\partial m_2}{\partial m_3}\right)_{\mu} + \left(\frac{\partial\rho}{\partial m_3}\right)_{m_2,P} + \left(\frac{\partial\rho}{\partial P}\right)_{m_2,m_3}\left(\frac{\partial P}{\partial m_3}\right)_{\mu} \quad (24)$$

However, in an actual experiment, the density is measured on a sample which has been withdrawn from the equilibrium cell and brought to the original pressure. The measured change in density (for a differential increase in concentration) is now the sum of two changes for two processes: (A) the increase of concentration at constant chemical potential; and (B) the reinstatement of original pressure, i.e.,

$$\mathrm{d}\rho = \mathrm{d}\rho_{\mathrm{A}} + \mathrm{d}\rho_{\mathrm{B}} \quad (25)$$

where

$$\mathrm{d}\rho_{\mathrm{A}} = \left(\frac{\partial\rho}{\partial m_2}\right)_{m_3,P}\mathrm{d}m_2 + \left(\frac{\partial\rho}{\partial m_3}\right)_{m_2,P}\mathrm{d}m_3 + \left(\frac{\partial\rho}{\partial P}\right)_{m_2,m_3}\mathrm{d}P_{\mathrm{A}} \quad (26)$$

$$\mathrm{d}\rho_{\mathrm{B}} = (\partial\rho/\partial P)_{m_2,m_3}\,\mathrm{d}P_{\mathrm{B}} \quad (27)$$

$$\mathrm{d}P_{\mathrm{B}} = -\mathrm{d}P_{\mathrm{A}} \quad (28)$$

Consequently,

$$\left(\frac{\partial\rho}{\partial m_3}\right)_{\mu^*,P} = \left(\frac{\partial\rho}{\partial m_2}\right)_{m_3,P}\left(\frac{\partial m_2}{\partial m_3}\right)_{\mu} + \left(\frac{\partial\rho}{\partial m_3}\right)_{m_2,P} \quad (29)$$

where the subscript μ^*,P denotes the combination of both processes. Thus, if the measurement of density of the solution is performed at the same pressure as used with the solvent, there is no necessity of introduction of the term

$$\left(\frac{\partial\rho}{\partial P}\right)_{m_2,m_3}\left(\frac{\partial P}{\partial m_3}\right)_{\mu} = \kappa\rho\,\frac{\mathrm{d}\pi}{\mathrm{d}m_3} \quad (30)$$

where κ is the isothermal compressibility coefficient and π is the osmotic pressure. Such a term has been routinely introduced into calculation and then neglected as insignificant.[10,58] It is worthwhile to note that the same argument applies for the measurement of the refractive index increments.

In the following, for simplicity, the subscript μ still will be used: it will mean the above defined subscript μ^*,P. Then the quantity of interest, $(\partial\rho/\partial c_3)_{\mu}$, can be obtained from the manipulation of eq 1–5 and 29 as

$$\left(\frac{\partial\rho}{\partial c_3}\right)_{\mu} = \frac{(1 - \bar{v}_3\rho) + (1 - \bar{v}_2\rho)(M_2/M_3)\,(\partial m_2/\partial m_3)_{\mu}}{\{1 - c_3[\bar{v}_3 + (M_2/M_3)\bar{v}_2\,(\partial m_2/\partial m_3)_{\mu}]\}} \quad (31)$$

In the limit of vanishing polymer concentration, eq 31 reads

$$\lim_{c_3\to 0}\left(\frac{\partial\rho}{\partial c_3}\right)_{\mu} \equiv \left(\frac{\partial\rho}{\partial c_3}\right)^{0} = (1 - \bar{v}_3{}^{0}\rho^{0}) + (1 - \bar{v}_2{}^{0}\rho^{0})\frac{M_2}{M_3}\left(\frac{\partial m_2}{\partial m_3}\right)_{\mu}^{0} \quad (32)$$

Therefore, the quantity $(\partial m_2/\partial m_3)_{\mu}{}^{0}$, which is a measure of the preferential adsorption, could be obtained from the combination of eq 32 and 23 as

$$\left(\frac{\partial m_2}{\partial m_3}\right)_{\mu}^{0} = \frac{M_3}{M_2}\,\frac{(\partial\rho/\partial c_3)_{m_2,P}{}^{0} - (\partial\rho/\partial c_3)_{\mu}{}^{0}}{\bar{v}_2{}^{0}\phi_1{}^{0}\,(\mathrm{d}\rho/\mathrm{d}\phi_1)^{0}} \quad (33)$$

During the above derivations, the identity eq 34 was used.

$$(1 - \bar{v}_2\rho^{0}) = -\bar{v}_2\phi_1{}^{0}\left(\frac{\mathrm{d}\rho}{\mathrm{d}\phi_1}\right)^{0} \quad (34)$$

The preferential adsorption is frequently described by parameter λ defined as

$$\lambda = -v_2{}^{0}\phi_1{}^{0}\,\frac{M_2}{M_3}\left(\frac{\partial m_2}{\partial m_3}\right)_{\mu}^{0} \quad (35)$$

Substitution of eq 33 to eq 35 gives

$$\lambda = \frac{[(\partial\rho/\partial c_3)_{\mu}{}^{0} - (\partial\rho/\partial c_3)_{m_2,P}{}^{0}]}{(\mathrm{d}\rho/\mathrm{d}\phi_1)^{0}} \quad (36)$$

Alternatively, the density increment at constant chemical potential, $(\partial\rho/\partial c_3)_{\mu}{}^{0}$, can be defined using the new quantity $\bar{v}_3{}^*$ in a similar expression as eq 23.

$$(\partial\rho/\partial c_3)_{\mu}{}^{0} \equiv 1 - \bar{v}_3{}^*\rho^{0} \quad (37)$$

It is convenient to call $\bar{v}_3{}^*$ the partial specific volume of polymer at constant chemical potential or apparent partial specific volume. Finally, expression 35 can be rewritten in terms of partial specific volume using eq 23 and 37.

$$\lambda = \frac{(\bar{v}_3 - \bar{v}_3{}^*)\rho^{0}}{(\mathrm{d}\rho/\mathrm{d}\phi_1)^{0}} \quad (38)$$

Thus, the preferential adsorption coefficient λ can be obtained by the measurement of partial specific volume at constant composition and at constant chemical potential. The former quantity $\bar{v}_3{}^{0}$ may be obtained by the measurements of density of polymer solutions and the latter quantity $\bar{v}_3{}^*$ can be measured by the sedimentation equilibrium experiment. It should be noted that in the light-scattering experiments, the parameter λ can be obtained from a similar expression through refractive index increment $(\partial n/\partial c_3)$ as shown in eq 39.

$$\lambda = \frac{(\partial n/\partial c_3)_{\mu}{}^{0} - (\partial n/\partial c_3)_{m_2,P}{}^{0}}{(\mathrm{d}n/\mathrm{d}\phi_1)^{0}} \quad (39)$$

Sedimentation Equilibrium. The basic condition of sedimentation equilibrium leads to the following two equations for a three-component system in the ultracentrifuge.

$$\left(\frac{\partial\mu_2}{\partial m_2}\right)_{m_3,P}\frac{\mathrm{d}m_2}{\mathrm{d}r} + \left(\frac{\partial\mu_2}{\partial m_3}\right)_{m_2,P}\frac{\mathrm{d}m_3}{\mathrm{d}r} = \omega^2 r M_2(1 - \bar{v}_2\rho) \quad (40)$$

$$\left(\frac{\partial\mu_3}{\partial m_2}\right)_{m_3,P}\frac{\mathrm{d}m_2}{\mathrm{d}r} + \left(\frac{\partial\mu_3}{\partial m_3}\right)_{m_2,P}\frac{\mathrm{d}m_3}{\mathrm{d}r} = \omega^2 r M_3(1 - \bar{v}_3\rho) \quad (41)$$

Here, r is the radial distance from axis of rotation and ω is the angular velocity of the rotor. The combination of eq 40, 41, and 10 leads to

$$\frac{\omega^2 r}{(\mathrm{d}m_3/\mathrm{d}r)} = \frac{(a_{33} - a_{23}{}^2/a_{22})}{M_3(1 - \bar{v}_3\rho) - (a_{23}/a_{22})M_2(1 - \bar{v}_2\rho)} \quad (42)$$

Equation 42 may be transformed to eq 43 by using eq 19, 34, and 35.

$$\frac{\omega^2 r}{(\mathrm{d}m_3/\mathrm{d}r)} = \frac{(a_{33} - a_{23}{}^2/a_{22})}{M_3[(1 - \bar{v}_3\rho) + \lambda\,\mathrm{d}\rho/\mathrm{d}\phi_1][1 - c_3(\bar{v}_3 + \lambda/\phi_1)]} \quad (43)$$

Manipulation of eq 43 by using eq 21, 32, and 37 leads further to

$$\frac{\omega^2 r}{RT\,(\mathrm{d}c_3/\mathrm{d}r)} = \frac{1}{(1 - \bar{v}_3{}^*\rho)} + \frac{2A_2c_3}{1 - \bar{v}_3{}^*\rho} \cdots \tag{44}$$

where the second virial coefficient A_2 represents the same quantity as in eq 21. Equation 44 has the same form as for single solvent systems; only $\bar{v}_3$ is replaced by the apparent partical specific volume term $\bar{v}_3{}^*$. Therefore, in data analysis the same techniques can be employed as used for single solvent systems.[60,61]

Thermodynamics of Three-Component Systems. The preferential adsorption coefficient λ and second virial coefficient A_2 can be explicitely computed if the analytical expression for Gibbs free energy of mixing ΔG_{mix} is known. Flory–Huggins theory of polymer solutions in mixed solvents is usually used for that purpose. However, the original Flory–Huggins expression is not satisfactory even for binary systems. Obviously, a more elaborate expression for ΔG_{mix} is needed.

In this study, we will use a strictly phenomenological completely general expression for ΔG_{mix}; relation 45 originally due to Pouchlý et al.[51] will be employed.

$$\Delta G_{\mathrm{mix}}/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_1)n_1\phi_2 + g_{13}(\phi_3)n_1\phi_3 + g_{23}(\phi_3)n_2\phi_3 + g_{\mathrm{T}}(u_1,\phi_3)n_1\phi_2\phi_3 \tag{45}$$

where

$$u_1 = \phi_1/(\phi_1 + \phi_2) \tag{46}$$

The binary interaction functions g_{12}, g_{13}, g_{23} encompass all the properties of the appropriate binary systems. Obviously, g_{13} and g_{23} are functions of molecular weight of the polymer. The ternary interaction function g_{T} encompasses all deviations from the idealized system, for which only the binary interactions are considered; eq 45 is actually a definition of g_{T}. Obviously, g_{T} is a function of the composition and of the molecular weight of the polymer.

To obtain the expressions for the second virial coefficient, A_2, and the preferential adsorption parameter, λ, according to eq 19 and 21, the second derivatives of ΔG_{mix}, i.e., a_{ij}, are needed. By the conventional derivation they are obtained in the following forms

$$a_{22}{}^0 = \frac{n_1}{n_2}\,\frac{\bar{V}_2RT}{\bar{V}_{\mathrm{m}}}b_{22} \tag{47}$$

$$a_{23}{}^0 = \frac{n_1\bar{V}_2\bar{V}_3RT}{\bar{V}_m{}^2}b_{23} \tag{48}$$

$$m_3a_{33}{}^0 - RT = \frac{n_3\bar{V}_3{}^2RT}{\bar{V}_m\bar{V}_1}b_{33} \tag{49}$$

where

$$b_{22} = \phi_1 l + \phi_2 - \phi_1\phi_2\left\{2\left[g_{12} + (\phi_1 - \phi_2)\,\frac{\partial g_{12}}{\partial u_1}\right] - \phi_1\phi_2\,\frac{\partial^2 g_{12}}{\partial u_1{}^2}\right\} \tag{50}$$

$$b_{23} = g_{23}{}^0 l - g_{13}{}^0 + 1 - l - (\phi_1 - \phi_2)(g_{12} - g_{\mathrm{T}}{}^0) + \phi_1\phi_2\left(\frac{\partial g_{12}}{\partial u_1} - \frac{\partial g_{\mathrm{T}}{}^0}{\partial u_1}\right) \tag{51}$$

$$b_{33} = \phi_1 + \phi_2 l + 2\phi_1\phi_2(g_{12} - g_{\mathrm{T}}{}^0) - 2(\phi_1\chi_{13}{}^0 + \phi_2 l\chi_{23}{}^0) - 2\chi_{\mathrm{T}}{}^0\phi_1\phi_2 \tag{52}$$

Here l is the ratio of molar volumes $\bar{V}_1/\bar{V}_2$. All the quantities on the right-hand side of eq 50–52 are taken in the limit of vanishing concentration of polymer. During the above derivations, the binary interaction parameters $\chi_{i3}{}^0$ were related with $g_{i3}{}^0$ as in single solvent systems,[60]

$$\chi_{i3}{}^0 = g_{i3} - \left(\frac{\partial g_{i3}}{\partial \phi_3}\right)^0 \tag{53}$$

Similarly, a ternary interaction parameter $\chi_{\mathrm{T}}{}^0$ was defined as

$$\chi_{\mathrm{T}}{}^0 = g_{\mathrm{T}}{}^0 - \left(\frac{\partial g_{\mathrm{T}}}{\partial \phi_3}\right)^0_{u_1} \tag{54}$$

By substitution of eq 47–49 to eq 21 and 35 the second virial coefficient A_2 and preferential adsorption coefficient λ are obtained in convenient expressions as

$$A_2 = \frac{\bar{v}_3{}^2}{2\bar{V}_1}\,\frac{b_{22}b_{33} - b_{23}{}^2\phi_1\phi_2}{b_{22}} \tag{55}$$

$$\lambda = \bar{v}_3\phi_1\phi_2\,(b_{23}/b_{22}) \tag{56}$$

The original Flory–Huggins relation generalized for three-component systems[63] is a special case of eq 45 where g_{T} is equal to zero and all g_{ij}'s are independent of composition (i.e., $g_{ij} = \chi_{ij}$). For this special case, eq 56 leads to a form originally derived by Read.[7]

$$\lambda = \bar{v}_3{}^0\phi_1\phi_2\,\frac{\chi_{12}l^{-1}(\phi_2 - \phi_1) + \chi_{23} - \chi_{13}l^{-1} + l^{-1} - 1}{\phi_1 + l^{-1}\phi_2 - 2\chi_{12}l^{-1}\phi_1\phi_2} \tag{57}$$

The expression for A_2, eq 55, is for this case transformed to

$$A_2 = \frac{\bar{v}_3{}^2}{\bar{V}_1}\,Y(\phi_1) \tag{58}$$

$$Y(\phi_1) \boxminus \frac{l - 2l\phi_1\chi_{13} - 2l\phi_2\chi_{23} + D\phi_1\phi_2}{2(l\phi_1 + \phi_2 - 2\phi_1\phi_2\chi_{12})} \tag{59}$$

$$D \equiv 2\chi_{12}\chi_{13} + 2l\chi_{12}\chi_{23} + 2l\chi_{13}\chi_{23} - \chi_{12}{}^2 - \chi_{13}{}^2 - \chi_{23}{}^2l^2 \tag{60}$$

Actually expression 59 is the same as that derived by Shultz and Flory[6] in the analysis of intrinsic viscosity in mixed solvents. For a special case of $l = 1$, eq 58–60 reduce to the form given by Scott.[2]

In the following section we will show how, at least in principle, all the phenomenological functions in eq 45 can be obtained from the experimental data.

Some of the binary parameters may be obtained from experiments on binary systems. For polymers in a single solvent i, relation 55 simplifies to

$$A_{2,i} = \frac{\bar{v}_3{}^2}{\bar{V}_i}(1/2 - \chi_{i3}{}^0) \tag{61}$$

Thus the values $\chi_{i3}{}^0$, which depend on molecular weight, are calculated from the second virial coefficient in the single solvent $A_{2,i}$. It is worthwhile to note that in single solvent experiments in dilute solution the g_{i3} term is always combined with its derivative as in eq 53; only $\chi_{i3}{}^0$ is accessible from such experiments. For obtaining the $g_{i3}{}^0$ term some thermodynamic measurement should be made over the whole range of polymer concentration up to the pure polymer.[60] Such measurements are not generally available.

The function g_{12} and its derivatives may be obtained from vapor–liquid equilibria of the solvent mixture. Unfortunately, such measurements, which must be made at constant temperature (the same as in other experiments), are extremely rare.

We will now show how the remaining functions $g_T{}^0(u_1)$, $\chi_T{}^0(u_1)$, and $(g_{13}{}^0 - lg_{23}{}^0)$ may be obtained from the experimental values of A_2 and λ, assuming that the function $g_{12}(u_1)$ is known. It should be noted that all the following relations refer to vanishing concentration of polymer; in this limit $u_1 = \phi_1$ and $u_2 = \phi_2$; we will use the ϕ symbols.

It is convenient to define a new experimentally accessible function $L(\phi_1)$ as

$$L(\phi_1) = \lambda/(\phi_1\phi_2\bar{v}_3) \tag{62}$$

Equation 56 is now transformed into

$$b_{23} = L(\phi_1)b_{22} \tag{63}$$

Substitution of eq 63 into eq 51 yields after some rearrangement

$$\frac{\mathrm{d}[\phi_1\phi_2(g_T{}^0 - g_{12})]}{\mathrm{d}\phi_1} = g_{23}{}^0 l - g_{13}{}^0 + 1 - l + L(\phi_1)b_{22} \tag{64}$$

Integrating eq 64 with respect to ϕ_1 within limits $\phi_1 = 0$ and $\phi_1 = \phi_1$ and recognizing that both $g_T{}^0$ and g_{12} remain finite for $\phi_1 = 0$ we obtain

$$\phi_1\phi_2(g_T{}^0 - g_{12}) = (g_{23}{}^0 l - g_{13}{}^0 + 1 - l)\phi_1 - \int_0^{\phi_1} L(\phi_1)b_{22}\mathrm{d}\phi_1 \tag{65}$$

Equation 65 taken at the limit $\phi_1 = 1$ ($g_T{}^0$ and g_{12} remain finite also at this limit) yields the following expression for $(g_{13}{}^0 - lg_{23}{}^0)$

$$(g_{13}{}^0 - lg_{23}{}^0) = (1 - l) - \int_0^1 L(\phi_1)b_{22}\,\mathrm{d}\phi_1 \tag{66}$$

Finally, eq 66 is substituted into eq 65, which gives after some rearrangement

$$g_T{}^0(\phi_1) = g_{12} + (1/\phi_2)\int_{\phi_1}^1 L(\phi_1)b_{22}\,\mathrm{d}\phi_1 - (1/\phi_1)\int_0^{\phi_1} L(\phi_1)b_{22}\,\mathrm{d}\phi_1 \tag{67}$$

Thus, the parameter $(g_{13}{}^0 - lg_{23}{}^0)$ and function $g_T{}^0(\phi_1)$ can both be obtained from the preferential adsorption data λ. Here, the quantities L and $g_T{}^0$ are functions of molecular weight of the polymer sample and composition of the solvent.

In the next step of our analysis eq 63 is combined with eq 55 to yield the experimental value of b_{33} as

$$b_{33} = 2\bar{V}_1A_2/\bar{v}_3{}^2 + L^2b_{22}\phi_1\phi_2 \tag{68}$$

The last unknown function $\chi_T{}^0(\phi_1)$ is now obtained from combined eq 52 and 68 as

$$\chi_T{}^0(\phi_1) = g_{12} - g_T{}^0 + \frac{1}{\phi_2}(\tfrac{1}{2} - \chi_{13}{}^0) + \frac{l}{\phi_1}(\tfrac{1}{2} - \chi_{23}{}^0) - \frac{\bar{V}_1A_2}{\bar{v}_3{}^2\phi_1\phi_2} - \frac{L^2b_{22}}{2} \tag{69}$$

or when eq 67 and 61 are employed, as

$$\chi_T{}^0(\phi_1) = \frac{1}{\phi_1\phi_2}\left[\phi_1\left(\frac{\bar{V}_1A_{2,1}}{\bar{v}_{3,1}{}^2} - \frac{\bar{V}_1A_2}{\bar{v}_3{}^2} - \int_{\phi_1}^1 L(\phi_1)b_{22}\,\mathrm{d}\phi_1\right) + \phi_2\left(\frac{l\bar{V}_2A_{2,2}}{\bar{v}_{3,2}{}^2} - \frac{\bar{V}_1A_2}{\bar{v}_3{}^2} + \int_0^{\phi_1} L(\phi_1)b_{22}\,\mathrm{d}\phi_1\right) - \frac{\lambda Lb_{22}}{2\bar{v}_3}\right] \tag{70}$$

Here, $A_{2,1}$, $A_{2,2}$ and $\bar{v}_{3,1}$, $\bar{v}_{3,2}$ are the second virial coefficient and partial specific volume in pure solvent 1 and 2, respectively.

Experimental Procedure and Results.

Polystyrene samples with narrow distribution of molecular weight were obtained from Pressure Chemical Co., Pittsburgh, Pa. The basic properties of these samples were reported in our previous papers.[60,61] The molecular weight measured by the sedimentation equilibrium method in benzene solutions was found to be 35600 for sample 7b, 117000 for sample 4b, and 372000 for sample 3b. The reagent grade benzene, cyclohexane, and ethyl acetate were used for preparation of the solvent mixtures. The composition of solvent is reported as a volume fraction before mixing.

The experimental values of $\bar{v}_3$ at constant composition were measured in our laboratory by Mr. Aminabhavi[64] using a D.M.A. 02C. digital precision density meter. His measurements were made on two polystyrene samples (4b, 3b) using two different concentrations (0.01, 0.02 g/mL) at 20 °C. He has not observed any dependence of partial specific volume $\bar{v}_3$ on the molecular weight and/or the concentration of polymer.[64]

The sedimentation equilibrium experiments were performed using Spinco Model E Ultracentrifuge at 20 °C and the high-speed (meniscus depletion) method. The experimental and evaluation techniques were essentially the same as reported previously.[59-61] The original concentration of polystyrene was 5-7 × 10^{-4} g/mL; 0.15 mL of solution and solvent, respectively, were injected into a Kel-F coated double sector cell creating a 4.5 mm long column. The concentration as a function of position in the cell was evaluated from interference photographs (using the automated reading method[62]) in units of fringes. These units were converted to standard units using the values of refractive increment $(\Delta n/c)_\mu$ obtained by the method of diffusion in the synthetic boundary cell.[13]

The experimental data were plotted in the coordinates $[\omega^2c_3r/RT\,(\mathrm{d}c_3/\mathrm{d}r)]^{1/2}$ vs. c_3. These plots were reasonably linear for all samples (Figure 1). (Note that in these coordinates the ordinate and intercept are independent of units of concentration.)

We have shown previously[59] that, for simple solvents, the intercept of the linear part of this plot represents $[M_3(1 - \bar{v}_3\rho]^{1/2}$ and the product of the slope and the intercept is equal to $A_2/(1 - \bar{v}_3\rho)$. For simple solvents, $\bar{v}_3$ is measured by densitometry; the method, consequently, yield M_3 and A_2. For polymers in mixed solvents, according to eq 43, the quentities $[M_3(1 - \bar{v}_3{}^*\rho)]^{1/2}$ and $A_2/(1 - v_3{}^*\rho)$ are obtained by such an analysis. From these quantities the values of $\bar{v}_3{}^*$ and A_2 were calculated using the values of molecular weight M_3 which were obtained through measurements in simple solvents. Since the sedimentation equilibrium experiments in simple solvents and in mixed solvents, respectively, were performed under analogous conditions, any systematic error due to a possible incorrect method of evaluation of molecular weight from the experimental data cancels out.

The values of the partial specific volume of polystyrene at constant chemical potential $\bar{v}_3{}^*$ are summarized together with corresponding values at constant composition, $\bar{v}_3{}^0$, in Tables I and II and plotted in Figures 2 and 3. The values of $(\mathrm{d}\rho/\mathrm{d}\phi_1)^0$ are also included in Tables I and II. The values of λ and L calculated according to eq 38 and 62 are collected in Tables III and IV and plotted in Figures 4-7. In Tables V and VI the values of the second virial coefficient are tabulated; they are plotted in Figures 8 and 9.

Discussion

Our experimental data of λ for benzene-cyclohexane systems are in reasonable agreement with much less detailed data measured by light scattering[7,8] and by the diffusion method.[12] However, the dependence of λ on molecular weight of polystyrene, which was repeatedly reported by Benoit and co-workers,[29-34] was not observed in our data.

For polystyrene in the ethyl acetate-cyclohexane mixture an inversion of the preferential adsorption is observed in the middle of the range of solvent composition. Such a behavior is expected in systems where two about equally good (or equally poor) solvents form a strongly nonideal mixture; this is the case of the above system. For the benzene-cyclohexane system an incipient inversion is

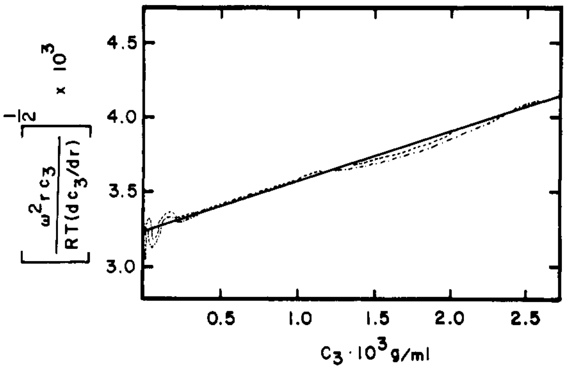

Figure 1. Plot of $[\omega^2 c_3 r/RT\ (dc_3/dr)]^{1/2}$ vs. c_3 for polystyrene sample 3b (mol wt = 372 000) in benzene (1)–cyclohexane (2) mixture with $\phi_2 = 0.5$ at 20 °C. The broken lines correspond to two different equilibrium photographs; the slope and intercept of the full straight line were used for data evaluation.

Table I
Partial Specific Volume of Polystyrene in Benzene (1)-Cyclohexane (2) Solvent Mixtures at 20 °C

ϕ_2	$\bar{v}_3$	$\bar{v}_3$* for sample			$(d\rho/d\phi_1)^0$
		7b	4b	3b	
0	0.914	0.914	0.914	0.914	0.1205
0.10	0.912	0.914	0.916	0.909	0.1172
0.20	0.912	0.912	0.913	0.910	0.1136
0.35	0.912[a]	0.910	0.909	0.907	0.1078
0.42	0.912[a]	0.903	0.907	0.902	0.1046
0.50	0.913	0.894	0.893	0.897	0.1014
0.60	0.914	0.892	0.896	0.891	0.0968
0.70	0.915	0.902	0.903	0.901	0.0921
0.80	0.917	0.910	0.908	0.909	0.0872
0.90	0.921	0.916	0.917	0.917	0.0819
1.00	0.925	0.923	0.928		0.0764

[a] Interpolated values.

Table II
Partial Specific Volume of Polystyrene in Ethyl Acetate (1)-Cyclohexane (2) Solvent Mixtures at 20 °C

ϕ_2	$\bar{v}_3$	$\bar{v}_3$* for sample			$(d\rho/d\phi_1)^0$
		7b	4b	3b	
0	0.912	0.913	0.911	0.913	−0.1582
0.10	0.909	0.917	0.915	0.913	−0.1508
0.20	0.908	0.923	0.919	0.919	−0.1445
0.35	0.907[a]	0.918	0.917	0.916	−0.1359
0.50	0.907	0.912	0.912	0.906	−0.1268
0.65	0.908[a]	0.901	0.899	0.893	−0.1154
0.80	0.913[a]	0.898	0.901	0.900	−0.1008
0.90	0.918	0.910	0.907	0.910	−0.0879
1.00	0.925	0.922	0.928		−0.0725

[a] Interpolated values.

Table III
Preferential Adsorption Coefficients λ and L for Polystyrene in Benzene (1)-Cyclohexane (2) Solvent Mixtures at 20 °C

ϕ_2	λ for sample			L for sample			L[a]
	7b	4b	3b	7b	4b	3b	
0							−0.13
0.10	−0.010	−0.027	0.020	−0.13	−0.33	0.24	−0.09
0.20	0.001	−0.010	0.018	0.01	−0.07	0.12	−0.02
0.35	0.013	0.019	0.038	0.06	0.09	0.18	0.16
0.42	0.072	0.041	0.082	0.32	0.18	0.37	0.30
0.50	0.148	0.159	0.126	0.65	0.70	0.55	0.60
0.60	0.180	0.151	0.189	0.82	0.69	0.86	0.80
0.70	0.114	0.105	0.123	0.59	0.55	0.64	0.63
0.80	0.065	0.079	0.075	0.44	0.54	0.51	0.51
0.90	0.043	0.036	0.041	0.52	0.43	0.50	0.46
1.00							0.44

[a] Smoothed data.

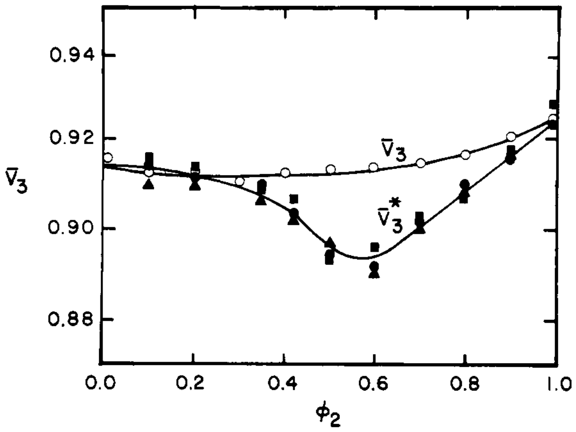

Figure 2. Partial specific volume of polystyrene in benzene (1)–cyclohexane (2) solvent mixtures as a function of solvent composition. Open points: values at constant composition of solvent $\bar{v}_3$. Full symbols: the apparent values $\bar{v}_3$*; ●, sample 7b, mol wt 35 600; ■, sample 4b, mol wt 117 000; ▲, sample 3b, mol wt 372 000. The line through the $\bar{v}_3$* values represents values calculated from the smoothed values of $\bar{v}_3$ and L.

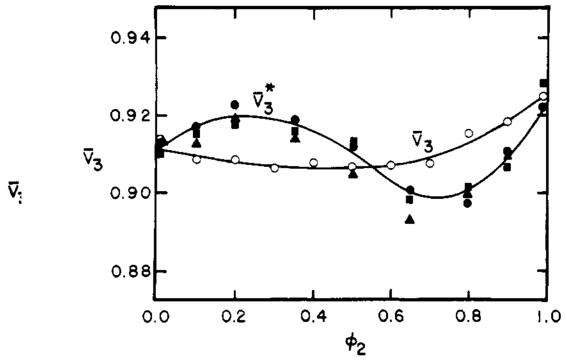

Figure 3. Partial specific volume of polystyrene in ethyl acetate (1)–cyclohexane (2) solvent mixtures. Same designation of points as in Figure 2.

Table IV
Preferential Adsorption Coefficients λ and L for Polystyrene in Ethyl Acetate (1)-Cyclohexane (2) Solvent Mixtures at 20 °C

ϕ_2	λ for sample			L for sample			L[a]
	7b	4b	3b	7b	4b	3b	
0							−0.42
0.10	−0.050	−0.036	−0.021	−0.61	−0.45	−0.26	−0.51
0.20	−0.088	−0.064	−0.067	−0.61	−0.44	−0.46	−0.51
0.35	−0.069	−0.060	−0.054	−0.34	−0.29	−0.26	−0.36
0.50	−0.031	−0.035	0.006	−0.14	−0.16	0.03	−0.10
0.65	0.053	0.066	0.105	0.26	0.32	0.51	0.26
0.80	0.116	0.093	0.101	0.79	0.64	0.69	0.66
0.90	0.076	0.100	0.077	0.90	1.21	0.93	0.96
1.00							1.24

[a] Smoothed data.

observed in mixtures rather rich in benzene. The poor solvent, cyclohexane, is preferentially adsorbed in this region. Similar behavior was observed for poly(methyl methacrylate) in a mixture of benzene and methanol;[17,36] methanol is preferentially adsorbed in mixtures where its volume fraction is 0.2 or less.

Our experimental values of second virial coefficient for all three samples depend on the composition of the solvent mixture in a quite similar way as does the intrinsic viscosity of the same samples reported by Munk et al.[50] Values of A_2 in the benzene–cyclohexane system decrease with increasing volume fraction of cyclohexane at first very slowly; later the decrease is very steep. For the ethyl acetate–

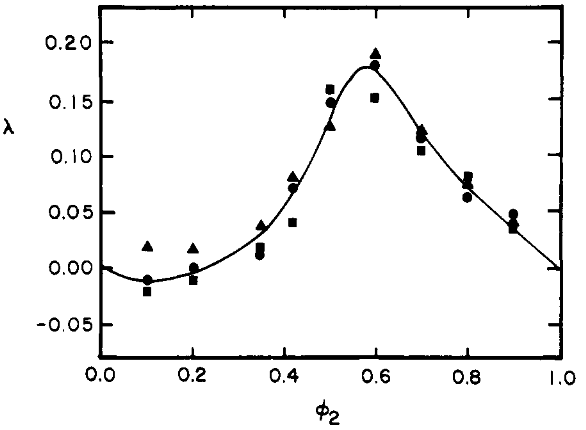

Figure 4. Coefficient of preferential adsorption λ for polystyrene in benzene (1)–cyclohexane (2) solvent mixtures as a function of solvent composition. The samples are designated by the same symbols as in Figure 2.

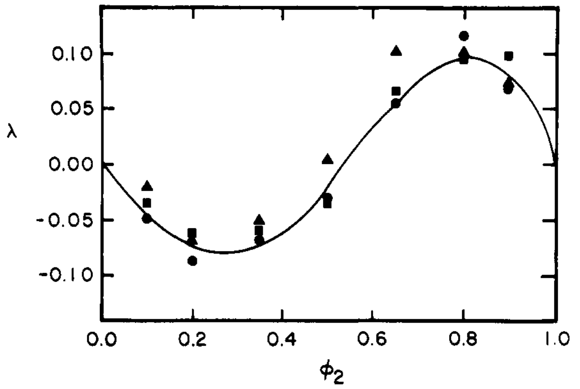

Figure 5. Coefficient of preferential adsorption λ for polystyrene in ethyl acetate (1)–cyclohexane (2) solvent mixtures as a function of solvent composition. The samples are designated by the same symbols as in Figure 2.

Table V
Second Virial Coefficient A_2 for Polystyrene in Benzene (1)-Cyclohexane (2) Solvent Mixtures at 20 °C

	$A_2 \times 10^4$ for sample (mol wt)		
ϕ_2	7b (35600)	4b (117000)	3b (372000)
0	6.83	5.30	3.68
0.10	6.34	5.16	3.72
0.20	5.36	5.22	3.54
0.35	4.68	3.48	3.22
0.42	4.29	4.35	3.19
0.50	4.46	4.31	2.87
0.60	3.21	3.48	2.60
0.70	1.91	2.73	2.02
0.80	0.00	1.56	1.50
0.90	−2.3	0.54	0.23
1.00	−3.8	−2.4	

Table VI
Second Virial Coefficient A_2 for Polystyrene in Ethyl Acetate (1)-Cyclohexane (2) Solvent Mixtures at 20 °C

	$A_2 \times 10^4$ for sample (mol wt)		
ϕ_2	7b (35600)	4b (117000)	3b (372000)
0	0.91	1.29	0.80
0.10	1.24	1.81	1.22
0.20	1.53	1.89	1.51
0.35	2.10	2.76	1.78
0.50	1.62	2.70	2.12
0.65	2.34	2.76	2.22
0.80	0.78	1.65	1.22
0.90	−0.6	0.41	0.40
1.00	−3.8	−2.4	

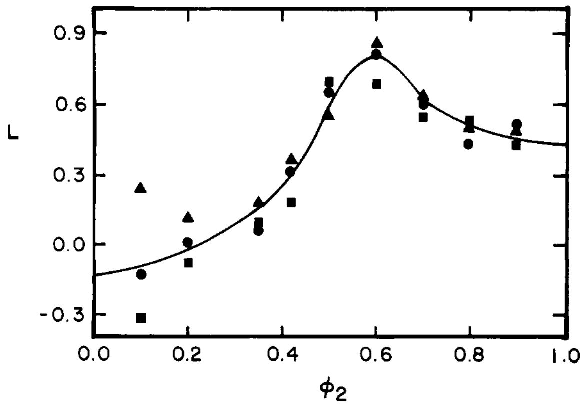

Figure 6. Parameter L for polystyrene in benzene (1)–cyclohexane (2) solvent mixtures. The same symbols as in Figure 2.

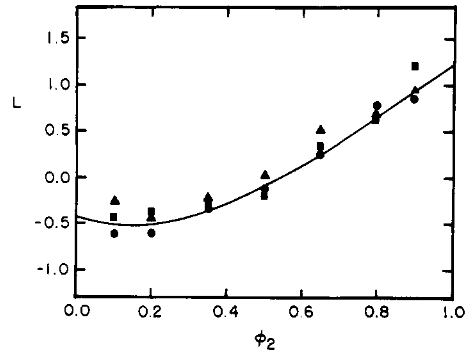

Figure 7. Parameter L for polystyrene in ethyl acetate (1)–cyclohexane (2) solvent mixtures. The same symbols as in Figure 2.

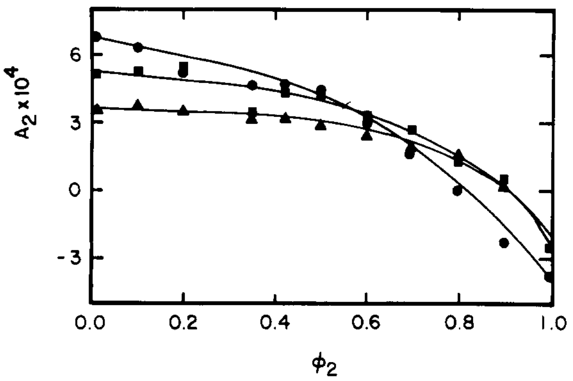

Figure 8. Second virial coefficient as a function of solvent composition for polystyrene in benzene (1)–cyclohexane (2) mixtures. The same symbols as in Figure 2.

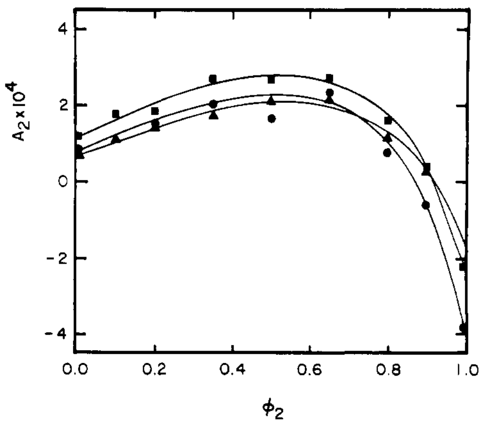

Figure 9. Second virial coefficient as a function of solvent composition for polystyrene in ethyl acetate (1)–cyclohexane (2) mixtures. The same symbols as in Figure 2.

Table VII
Interaction Parameters for Polystyrene in Mixed Solvents

solvent mixture	sample	$\chi_{13}{}^0$	$\chi_{23}{}^0$	$\chi_{13}{}^0 - l\chi_{23}{}^0$	$(g_{13}{}^0 - lg_{23}{}^0)^a$	$(g_{13}{}^0 - lg_{23}{}^0)^b$
benzene (1)–cyclohexane (2)	7b	0.427	0.549	−0.024	−0.098	−0.077
	4b	0.444	0.530	−0.008		
	3b	0.461	0.522[c]	0.032		
ethyl acetate (1)–cyclohexane (2)	7b	0.489	0.549	−0.008	0.037	0.015
	4b	0.485	0.530	0.004		
	3b	0.491	0.522[c]	0.017		

[a] Using g_{12} as defined by eq 71 and 72. [b] Using $g_{12} = 0.49$ for B–CH and $g_{12} = 1.00$ for EA–CH. [c] Estimated value.

cyclohexane system the values of A_2 exhibit a maximum at the volume fraction of cyclohexane equal to about 0.6.

The dependence of A_2 on the molecular weight of polystyrene is somehow obscured by anomalous behavior of the low molecular weight sample 7b. For good solvents (e.g., benzene with up to 60% of cyclohexane) the value of A_2 decreases with increasing molecular weight as is expected according to theories of excluded volume.[65] For marginal solvents (benzene with more than 60% of cyclohexane and all ethyl acetate–cyclohexane mixtures) the same behavior is still observed for the two higher molecular weight samples. However, with the solvent getting poorer, the value of A_2 for sample 7b decreases faster than do the values for the other samples. It first gets lower than the value for sample 4b; with still poorer solvents, it is even lower than the value for sample 3b. Similar anomaly was also found in the analysis of viscometric results;[50] the Huggins constant of the same sample 7b has appreciably higher value than those of other samples in the same marginal solvents. At the present time we have no explanation for this effect. Perhaps there is some chemical difference in the samples; the presence of few polar groups may influence aggregation in marginal solvents while exhibiting no effect in good solvents.

For the evaluation of our experimental data, we tried first to employ the simple relation for ΔG_{mix}, which led to eq 57–60. When plausible values of the coefficients χ_{ij} were used, the shape of the dependence of preferential adsorption λ on the composition of the solvent mixture was predicted quite correctly. For the benzene–cyclohexane system the values of λ were generally underestimated by a factor of 2 or less; for the ethyl acetate–cyclohexane system they were overestimated by a similar factor. However, for any plausible values of χ_{12} relations 58–60 predicted high maximum of the dependence of second virial coefficient A_2 on solvent composition. In the region of the maximum the virial coefficients were overestimated by a factor of 3 in the benzene–cyclohexane system and by a factor of 10 in the ethyl acetate–cyclohexane system. A similar discrepancy was observed in the viscometric behavior of the same systems.[50]

Because the oversimplified relation for ΔG_{mix} did not lead to acceptable interpretation of our data, we tried to employ the approach, outlined in the theoretical part, for evaluation of the phenomenological functions. The main problem encountered in this evaluation is the fact that the function g_{12} and its derivatives are not available. However, their values at higher temperature (approximately 80 °C) can be calculated from the activity coefficient data which were measured by Chao and Hougen[66] using the vapor–liquid equilibrium at atmospheric pressure. We have evaluated their data to yield for the benzene (1)–cyclohexane (2) mixture

$$g_{12} = 0.303 + 0.704\phi_2 - 0.057\phi_2{}^2 \qquad (71)$$

and for the ethyl acetate (1)–cyclohexane (2) mixture

$$g_{12} = 0.753 + 0.209\phi_2 - 0.018\phi_2{}^2 \qquad (72)$$

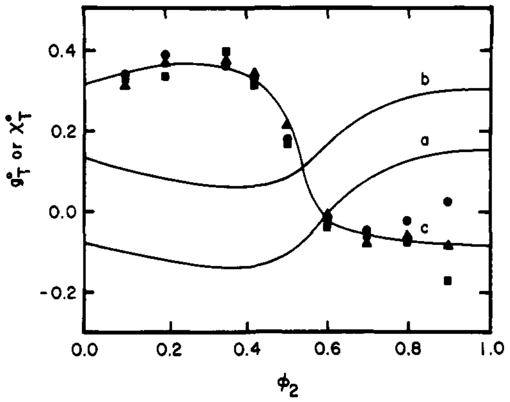

Figure 10. Polystyrene in mixtures of benzene (1) and cyclohexane (2). Parameter $g_T{}^0$ as a function of solvent composition when g_{12} is given by eq 71 (curve a); $g_{12} = 0.49$ (curve b). Experimental points and curve c represent parameter $\chi_T{}^0$. The same symbols as in Figure 2.

Since we have not detected any clear dependence of the preferential adsorption parameters λ and L on molecular weight we have drawn a single smooth line through the experimental values of L for all three polystyrene samples in Figures 6 and 7. The integrals in eq 66–70 were evaluated numerically using this smooth line. The smooth line is reported in Tables III and IV. It is a consequence of L being assumed independent of molecular weight that the functions $(g_{13}{}^0 - g_{23}{}^0)$ and $g_T{}^0$ are also independent of molecular weight. This result is not implausible in spite of the fact that the corresponding values of $(\chi_{13}{}^0 - l\chi_{23}{}^0)$, which are reported in Table VII, do depend clearly on molecular weight. It is quite possible, and the excluded volume theory as formulated by Koningsveld et al.[67] seems to indicate,[60] that $g_{i3}{}^0$ is fairly independent of molecular weight; it is its derivative $(\partial g_{i3}/\partial\phi_3)^0$ which varies strongly with molecular weight (cf. eq 53).

Lacking the appropriate data at 20 °C, we have used for g_{12} the functions represented by eq 71 and 72; from them the values of b_{22} were obtained using eq 50; these values, in turn, were used for calculation of integrals in eq 66–70. To get some insight into the sensitivity of the calculation toward the selection of g_{12} we repeated the calculations using arbitrary constant values. The plausible values $g_{12} = 0.49$ for the benzene–cyclohexane mixture and $g_{12} = 1.0$ for the ethyl acetate–cyclohexane mixture were selected. The resulting function $g_T{}^0$ is plotted as a function of solvent composition in Figures 10 and 11. The values of $(g_{13}{}^0 - lg_{23}{}^0)$ are reported in Table VII together with other values pertinent to the evaluation of our data. The results are rather sensitive to the choice of g_{12} values indicating the necessity of obtaining more reliable data for the latter.

Once the preferential adsorption data have been evaluated, the value of $\chi_T{}^0$ for each experiment may be calculated from the second virial coefficient using eq 69 and 70. The values of $\chi_T{}^0$ are presented in Figures 10 and 11. The values depend on the choice of g_{12}, but the dependence

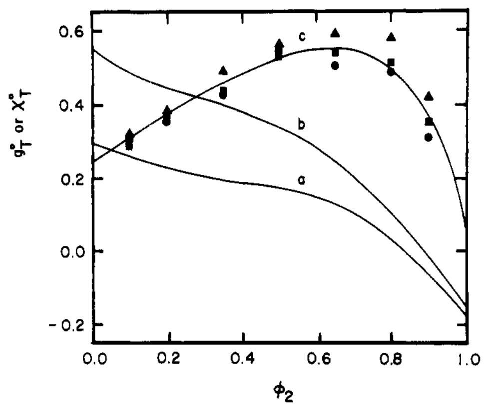

Figure 11. Polystyrene in mixtures of ethyl acetate (1) and cyclohexane (2). Parameter g_T^0 as a function of solvent composition when g_{12} is given by eq 72 (curve a); $g_{12} = 1.00$ (curve b). Experimental points and curve c represent parameter χ_T^0. The same symbols as in Figure 2.

is much smaller than in the case of the function g_T^0. In fact, all plausible functions g_{12} lead to values of χ_T^0 which exhibit among themselves differences that are smaller than the inherent experimental error. Consequently, we feel that it is safe to conclude that the necessity of introduction of the ternary function χ_T^0 (and by virtue of eq 54 also g_T^0) has been clearly established.

The second virial coefficient A_2 depends significantly on molecular weight. However, the dependence (including the anomalous behavior of sample 7b) is almost fully accounted for by assigning the proper values to the binary constants χ_{i3}^0; these values were obtained directly from the virial coefficients measured in pure solvents. The values of χ_T^0 vary systematically with molecular weight, but the differences between the samples are not much above the experimental error. Consequently, we have represented χ_T^0 for all three samples by a single line in Figures 10 and 11.

The form of the interaction functions g_T^0 and χ_T^0 as derived from our experiments is rather complex. Since no theory of these functions is available, the interpretation of them has to be left for future study.

Conclusions

The preferential adsorption coefficient λ and second virial coefficient A_2 for three polystyrene samples in two solvent mixtures have been measured by the sedimentation equilibrium technique over the whole range of composition of these solvent mixtures.

An inversion of the preferential adsorption has been observed in the ethyl acetate–cyclohexane mixture. An incipient inversion was also observed in a mixture of a very good solvent (benzene) with a rather poor one (cyclohexane). Thus, it seems that the inversion is a rather common phenomenon.

The original Flory–Huggins expression for free energy of mixing (generalized for three components), which is traditionally used for interpretation of experiments in mixed solvents, led to a very poor agreement between theory and experiment when used for simultaneous interpretation of values of λ and A_2. Consequently, a completely general phenomenological expression for ΔG_{mix}, eq 45, was employed. The rigorous analysis of the data was prevented by the lack of a suitable expression for the free energy of mixing of the solvent components themselves. Nevertheless, it has been shown that the introduction of the ternary functions g_T^0 and χ_T^0 is necessary for plausible interpretation of experimental data.

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Viscoelastic Properties of Linear Polymers with High Molecular Weights and Sharp Molecular Weight Distributions

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ABSTRACT: Viscoelastic properties of concentrated solutions of linear polystyrenes having high molecular weights and sharp moleculcar weight distributions were studied by a Weissenberg rheogoniometer and also by a torsional creep apparatus of the Plazek type. Dynamic modulus and creep compliance of those samples were determined as functions of frequency and time, respectively. It was confirmed that there are two different relaxation mechanisms in the viscoelastic behavior of concentrated solutions of linear polymers. The separation of two mechanisms appears clearer in this study than in other studies, due to the high molecular weights of our samples. Deviation from the WLF equation on the temperature dependence of shift factor was found at high temperatures.

It is generally accepted that viscoelastic properties of concentrated solutions and the melts of linear polymers are governed by two types of relaxation mechanisms: the intramolecular motions of segments and the molecular motions involving the adjustments and the shifting of chain entanglements.[1-3] The two mechanisms should have quite different characteristics and the relaxation times corresponding to the two mechanisms should be unrelated. That is, relaxation times involving intramolecular interactions are independent of molecular weight, whereas the relaxation times showing molecular motions depend on molecular weight.[6-9]

The presence of the two mechanisms can be observed as the appearance of the plateau region in the storage modulus vs. frequency plot or in the creep compliance vs. time plot. That is, a minimum is observed in the relaxation or retardation spectra.[4-9] These features are expected to become clearer with increasing molecular weight.

The purpose of this work is to study such viscoelastic properties of linear polymer solutions in the plateau and terminal zones, using the polystyrenes having high molecular weights and narrow molecular weight distributions.

Moreover, if these two relaxation mechanisms are separated enough, the temperature dependence of the shift factor for time–temperature superposition would not necessarily be the same in both regions, as was pointed out by Sōen, Ono, Yamashita, and Kawai.[10] Nevertheless, the shift factors reported in the literature were always well expressed by the WLF equation.[2] It is also our purpose to clarify this problem using samples having high molecular weights and narrow molecular weight distributions.

Table I

sample no.	M_w	M_w/M_n	C, g/dL
201	1.4×10^6	1.02[a]	10.5
			20.9
			26.4
			102 (undiluted)
002	1.1×10^7		11.7
			15.8
			56.4
			72.0
			80.8
401	1.2×10^7		7.92
			15.5

[a] The values calculated from the molecular weight distribution curve determined by the sedimentation-velocity method.[11]

Experimental Section

Samples. Nearly monodisperse polystyrene samples were prepared by an anionic polymerization method as described in a previous paper.[11] Low and high molecular weight tails of these samples were removed by fractional precipitation from their benzene solutions with addition of methanol. Samples no. 002 and 401 have high molecular weights, while sample no. 201 has an ordinary molecular weight. The molecular weights of these samples are listed in Table I. The weight average molecular weights of the samples were determined by the light-scattering method in *trans*-decalin at 22 °C (Θ temperature) or 30 °C and in cyclohexane at 35 °C (Θ temperature) using a light-scattering photometer, Fica-50. The molecular weight distributions of the samples were checked by the sedimentation-velocity method in cyclohexane at 35 °C using an analytical ultracentrifuge, Beckmann Spinco Model E. The molecular weights of samples no. 002 and 401 were so high that it was difficult to determine their molecular weight distributions by the sedimentation-velocity method. At least, however, it may be concluded from the sedimentation patterns in Figure 1 that the molecular weight dis-

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