Preferential Adsorption onto Polystyrene in Mixed Solvent Systems

Tejraj M. Aminabhavi and Petr Munk*

Department of Chemistry, The University of Texas, Austin, Texas 78712.

Received February 15, 1979

ABSTRACT: A previously developed technique using the ultracentrifuge as a differential refractometer has been modified and applied for the evaluation of preferential adsorption onto polymers. Three polystyrene samples in two combinations of solvent mixtures, benzene (1)–cyclohexane (2) and ethyl acetate (1)–cyclohexane (2), were measured over the entire range of composition of the solvent mixture. Semiempirical relations were developed for the binary solvent interaction parameter, g_{12}, as a function of temperature and solvent composition. The experimental results are discussed in relation to preferential adsorption, thermodynamical interaction parameters, and excess free energy of mixing of the two liquid components. The results confirmed and refined the conclusions drawn from sedimentation equilibrium experiments for the same experimental system.

When a polymer is dissolved in a binary solvent mixture, usually one of the solvents preferentially solvates the polymer. From this preferential adsorption, thermodynamical interaction parameters may be calculated. The extent of preferential adsorption of solvents can be derived from the measurements of refractive index.

For the measurement of preferential adsorption, we employed our previously developed diffusion technique[1] in a synthetic boundary cell in the ultracentrifuge. Three polystyrene samples with narrow distribution of molecular weights dissolved in two combinations of binary solvent mixtures, benzene–cyclohexane and ethyl acetate–cyclohexane, were used. The whole range of compositions of these mixtures was studied.

Earlier work[2] on these ternary systems has indicated that the behavior of polymer in a mixed solvent is influenced largely by the thermodynamic properties of the binary liquid mixture. In that earlier study, tentative expressions for binary solvent-interaction parameter g_{12} were employed. In the present study, special attention is devoted to the detailed thermodynamic analysis of binary solvent mixtures and to the evaluation of the phenomenological function g_{12} expressed as a function of temperature and composition of the mixture. The resulting relations are incorporated into the expression for ΔG_{mix} for our ternary systems. The phenomenon of preferential adsorption is discussed in terms of the phenomenological interaction parameters in a three component system.

Theoretical

The phenomenon of preferential adsorption is best understood in terms of membrane equilibrium. At equilibrium, the chemical potentials of both solvent components should be the same on both sides of a semipermeable membrane. In the presence of a nondiffusible (polymer) species on one side of the membrane, this condition leads not only to the establishment of the osmotic pressure but also to a different composition of the solvent on both sides of the membrane. The preferential adsorption is conveniently described as the change of molality of one of the solvent components due to the presence of the nondiffusible species, $(\partial m_2/\partial m_3)^0_\mu$.

In our present notation, the indices 1 and 2 are used for the solvent components, and the index 3 is used for macromolecules. The subscript μ means constant chemical potential of both solvent components; the superscript zero designates the limit of zero concentration of the polymer. The symbols M_i, n_i, x_i, m_i, c_i, and ϕ_i represent respectively molecular weight, number of moles, molar fraction, molality, concentration (in g/mL), and volume fraction before mixing of the ith component. Different concentration units are related to each other as

$$x_i = n_i/\sum_j n_j \tag{1}$$

$$m_i = 1000n_i/n_1M_1 \tag{2}$$

$$c_i = n_iM_i/\bar{V} \tag{3}$$

$$\phi_i = n_iV_i/V \tag{4}$$

$$\bar{V} = \sum_j n_j\bar{V}_j \tag{5}$$

$$V = \sum_j n_jV_j \tag{6}$$

Here, V and $\bar{V}$ are the total volumes of solutions before mixing and after mixing, respectively. Similarly, V_i and $\bar{V}_i$ denote molar volume of pure component i and its partial molar volume, respectively; corresponding specific volumes are v_i and $\bar{v}_i$.

In our three-component system, the following relation may be written for a change of any intensive property y with concentration of polymer

$$\left(\frac{\partial y}{\partial c_3}\right)^0_\mu = \left(\frac{\partial y}{\partial c_3}\right)^0_{m_2,P} + \left(\frac{\partial y}{\partial m_2}\right)^0_{m_3,P}\left(\frac{\partial m_2}{\partial m_3}\right)^0_\mu\left(\frac{\partial m_3}{\partial c_3}\right)^0_\mu + \left(\frac{\partial y}{\partial P}\right)_{m_2,m_3}\left(\frac{\partial P}{\partial c_3}\right)^0_\mu \tag{7}$$

In our previous paper,[2] we have shown that the last term of eq 7 disappears when the property y is measured on a sample which was withdrawn from the equilibrium cell and brought to the original pressure. In that paper,[2] we have applied relation 7 to the case where y is the density. In the present paper, we study the refractive index n of the mixture. For this case (and neglecting the pressure term), eq 7 transforms into:

$$\left(\frac{\partial n}{\partial c_3}\right)^0_\mu = \left(\frac{\partial n}{\partial c_3}\right)^0_{m_2,P} + \left(\frac{\partial n}{\partial m_2}\right)^0_{m_3,P}\left(\frac{\partial m_2}{\partial m_3}\right)^0_\mu\left(\frac{\partial m_3}{\partial c_3}\right)^0_\mu \tag{8}$$

The quantity $(\partial m_2/\partial m_3)^0_\mu$, which is a measure of the preferential adsorption, could be obtained from eq 8 as:

$$\left(\frac{\partial m_2}{\partial m_3}\right)^0_\mu = \frac{(\partial n/\partial c_3)^0_\mu - (\partial n/\partial c_3)^0_{m_2,P}}{(\partial n/\partial m_2)^0_{m_3,P}\,(\partial m_3/\partial c_3)^0_\mu} \tag{9}$$

It is convenient to define a new quantity λ as

$$\lambda \equiv -\left(\frac{\partial m_2}{\partial m_3}\right)^0_\mu \phi_1 v_2 \frac{M_2}{M_3}\frac{\bar{V}_0}{V_0} \tag{10}$$

Substituting eq 9 into eq 10 and recognizing that

0024-9297/79/2212-0607$01.00/0

$$(\partial n/\partial m_2)^0_{m_3,P} = -(\mathrm{d}n/\mathrm{d}\phi_1)^0\phi_1 v_2 M_2/V^0 \qquad (11)$$

and

$$(\partial m_3/\partial c_3)^0_\mu = \bar{V}^0/M_3 \qquad (12)$$

we finally get

$$\lambda = \frac{(\partial n/\partial c_3)^0_\mu - (\partial n/\partial c_3)^0_{m_2,P}}{(\mathrm{d}n/\mathrm{d}\phi_1)^0} \qquad (13)$$

Thus, the coefficient of preferential adsorption λ may be obtained by the measurement of the refractive increment of the polymer at constant composition of the solvent mixture and at constant chemical potential. The quantity $(\mathrm{d}n/\mathrm{d}\phi_1)^0$ is measured on solvent mixtures in the absence of polymer. It should be noted that an equivalent of eq 13 is often used in light-scattering experiments.[3]

Thermodynamics of Three-Component Systems

The thermodynamic analysis of mixtures usually starts from the free enthalpy (Gibbs free energy) of mixing, ΔG_{mix}, expressed as a function of composition of the mixture. For our three-component system, we have evaluated the data using for ΔG_{mix} the phenomenological relation:[2]

$$\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2 g_{12} + n_1\phi_3 g_{13} + n_2\phi_3 g_{23} + n_1\phi_2\phi_3 g_{\mathrm{T}}] \qquad (14)$$

Here, R is the gas constant and T is the absolute temperature. The binary interaction parameters g_{13} and g_{23} are functions of the volume fraction of the polymer ϕ_3; they describe the thermodynamics of polymer solutions in pure solvents. The parameter g_{12} describes the behavior of a pure solvent mixture; it is a function of its volume fraction $u_1 \equiv \phi_1^0 = \phi_1/(\phi_1 + \phi_2)$. The ternary parameter g_{T} encompasses all deviations of the real system from the idealized system for which only the binary terms are considered. In fact, eq 14 is a definition of g_{T}.

In our previous study[2] we have defined the binary interaction parameters χ_{i3} and a ternary interaction parameter χ_{T} as

$$\chi_{i3} = g_{i3} - (\partial g_{i3}/\partial \phi_3) \qquad (15)$$

$$\chi_{\mathrm{T}} = g_{\mathrm{T}} - (\partial g_{\mathrm{T}}/\partial \phi_3)_{\phi_1} \qquad (16)$$

The parameter χ_{i3} is actually the well-known Flory–Huggins parameter for polymer in single solvent i. Its limiting value $\chi_{i3}{}^0$, which depends on the molecular weight of polymer, is calculated from the second virial coefficient $A_{2,i}$ of the polymer in a single solvent i using the relation

$$A_{2,i} = (\bar{v}_3{}^2/V_i)(1/2 - \chi_{i3}{}^0) \qquad (17)$$

The phenomenological parameters $g_{\mathrm{T}}{}^0$ and $\chi_{\mathrm{T}}{}^0$ are functions of the molecular weight of the polymer and composition of the solvent mixture. They may be calculated from experimental data using the following relations, which were derived in our previous paper.[2]

$$g_{\mathrm{T}}{}^0(\phi_1) = g_{12} + (1/\phi_2)\int_{\phi_1}^{1} L(\phi_1)b_{22}\,\mathrm{d}\phi_1 - (1/\phi_1)\int_0^{\phi_1} L(\phi_1)b_{22}\,\mathrm{d}\phi_1 \qquad (18)$$

$$\chi_{\mathrm{T}}{}^0(\phi_1) = g_{12} - g_{\mathrm{T}}{}^0 + (1/\phi_2)(1/2 - \chi_{13}{}^0) + (l/\phi_1)(1/2 - \chi_{23}{}^0) - \bar{V}_1 A_2/\bar{v}_3{}^2\phi_1\phi_2 - L^2 b_{22}/2 \qquad (19)$$

$$b_{22} = \phi_1 l + \phi_2 - \phi_1\phi_2[2g_{12} + 2(\phi_1 - \phi_2)\,(\mathrm{d}g_{12}/\mathrm{d}u_1) - \phi_1\phi_2\,(\mathrm{d}^2 g_{12}/\mathrm{d}u_1{}^2)] \qquad (20)$$

$$L(\phi_1) = \lambda/(\phi_1\phi_2\bar{v}_3) \qquad (21)$$

$$l = V_1/V_2 \qquad (22)$$

Here, A_2 is the second virial coefficient measured in the mixed solvent. The expression $(g_{13}{}^0 - lg_{23}{}^0)$ is obtained from the relation

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

Thus, the values of $(g_{13}{}^0 - lg_{23}{}^0)$ and $g_{\mathrm{T}}{}^0(\phi_1)$ may be obtained from the preferential adsorption data provided the interaction function for the solvent mixture $g_{12}(\phi_1)$ is known. For the calculation of values of $\chi_{\mathrm{T}}{}^0$, the second virial coefficients in the pure solvents and in the mixed solvent are needed.

Evaluation of the Binary Function g_{12}

The function g_{12} is needed at the temperature at which the values of A_2 and L have been measured. Measurements of vapor–liquid equilibria at our experimental temperature 20 °C are virtually nonexistent in the literature. However, if the vapor–liquid equilibrium is measured at some other temperature (usually much higher) and if the data for the enthalpy of mixing (calorimetric data) as a function of temperature are available, the desired g_{12} function may be obtained from Gibbs–Helmholtz equation

$$[\partial(\Delta G_{\text{mix}}/T)/\partial(1/T)]_{P,n_i} = \Delta H_{\text{mix}} \qquad (24)$$

The experimental values of ΔH_{mix} are usually presented for 1 mol of the mixture. It is convenient to express them by a function h_{12} defined as

$$\Delta H_{\text{mix}} \equiv x_1\phi_2 R h_{12} \qquad (25)$$

h_{12} is a function of the temperature and the composition of the mixture. For ΔG_{mix} we will use eq 14 written for a two-component system and 1 mol of the mixture as

$$\Delta G_{\text{mix}} = RT[x_1 \ln \phi_1 + x_2 \ln \phi_2 + x_1\phi_2 g_{12}] \qquad (26)$$

The substitution of eq 25 and 26 into eq 24 leads to

$$(\partial g_{12}/\partial(1/T))_{P,n_i} = h_{12} \qquad (27)$$

Benzene (1)–Cyclohexane (2) Mixture. Scatchard et al.[4] have measured vapor–liquid equilibria for this mixture at 40 and 70 °C for several compositions and also at a few other temperatures for one composition of the mixture. They expressed the results through the excess quantity F^{E}, which is related to our quantities as

$$F^{\mathrm{E}} = \Delta G_{\text{mix}} - RT(x_1 \ln x_1 + x_2 \ln x_2) \qquad (28)$$

Thus their experimental values of g_{12} could be obtained from combined eq 26 and 28. Chao and Hougen[5] have published activity coefficients γ_1 and γ_2 at the boiling point at 1 atm for several compositions of the mixture. ΔG_{mix} is related to activity coefficients as

$$\Delta G_{\text{mix}} = RT(x_1 \ln x_1\gamma_1 + x_2 \ln x_2\gamma_2) \qquad (29)$$

Thus combination of eq 26 and 29 yields their experimental values of g_{12}. Elliott and Wormald[6] have measured ΔH_{mix} for the benzene–cyclohexane mixture as a function of temperature and composition. Their data were converted to values of h_{12} using eq 25.

We have found that all the above data may be expressed by the empirical relations

$$h_{12} = h(T)f(\phi) \qquad (30)$$

$$g_{12} = g(T)f(\phi) \qquad (31)$$

Here, $h(T)$ and $g(T)$ are functions of temperature and $f(\phi)$ is a function of composition, which within the experimental error is independent of temperature and is applicable for both the enthalpy and free enthalpy data. From the

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

		$(\partial n/\partial c_3)^0_{m_2,P}$ at wavelengths		$(\partial n/\partial c_3)^0_\mu$ for sample			
ϕ_2	$\bar{v}_3$	546 nm	436 nm	4b	3b	13a	$(dn/d\phi_1)^0$
0.00	0.914	0.1034	0.1068	0.1024	0.1049	0.1037	0.0909
0.10	0.912	0.1126	0.1164	0.1118	0.1113	0.1107	0.0886
0.20	0.912	0.1200	0.1258	0.1203	0.1196	0.1190	0.0861
0.30	0.911	0.1292	0.1353	0.1308	0.1326	0.1316	0.0835
0.40	0.913	0.1350	0.1440	0.1402	0.1396	0.1399	0.0807
0.50	0.913	0.1421	0.1513	0.1521	0.1532	0.1512	0.0778
0.60	0.914	0.1482	0.1580	0.1602	0.1591	0.1582	0.0747
0.70	0.915	0.1543	0.1648	0.1623	0.1637	0.1613	0.0715
0.80	0.917	0.1585	0.1707	0.1651	0.1628	0.1639	0.0681
0.90	0.921	0.1624	0.1750	0.1646	0.1662	0.1648	0.0646
1.00	0.925	0.1662	0.1795	0.1660			0.0610

equilibrium data of Scatchard et al.[4] at 40 °C, which exhibited the least scatter, we have evaluated the function $f(\phi)$ as

$$f(\phi) = [1 + 0.038(\phi_2 - \phi_1) + 0.030(\phi_2 - \phi_1)^2] \quad (32)$$

Using eq 30 and 32, we have calculated the experimental values of $h(T)$ from the data of Elliott and Wormald.[6] The data suggested that $h(T)$ is a linear function of $(1/T)$; the least-squares analysis yielded

$$h(T) = (1.23 \times 10^5/T - 64.2) \quad (33)$$

The combined relations 30, 32, and 33 reproduced all the calorimetric data within 2.5% (maximum deviation). Substitution of eq 30, 31, and 33 into eq 27 yielded upon integration

$$g(T) = g^0 - 64.2/T + 6.15 \times 10^4/T^2 \quad (34)$$

The integration constant g^0 was evaluated from experimental values of g_{12} and T using eq 31, 32, and 34 for each vapor–liquid equilibrium. The best value of g^0 was 0.008 leading to our final expression for g_{12}

$$g_{12} = [0.008 - 64.2/T + 6.15 \times 10^4/T^2] \times [1 + 0.038(\phi_2 - \phi_1) + 0.030(\phi_2 - \phi_1)^2] \quad (35)$$

This relation reproduced the Scatchard et al.[4] experimental values of g_{12} within 0.5%. The values of Chao and Hougen[5] were on the average about 3% higher than values from eq 35.

Ethyl Acetate (1)–Cyclohexane (2) Mixture. The thermodynamic data for this mixture are rather scarce. The enthalpy of mixing at 25 °C was reported by Grolier and Villard[7] for several compositions. Least-squares analysis of their data led to the relation

$$h_{12}(25\ ^\circ\mathrm{C}) = 585.9[1 + 0.205(\phi_2 - \phi_1) + 0.265(\phi_2 - \phi_1)^2] \quad (36)$$

which reproduced the original data with maximum deviation of 1%. However, the authors themselves claim that the standard deviation is about 5%.

Chao and Hougen[5] published activity coefficients at the boiling point at 1 atm for several compositions. The values of g_{12} were obtained from them using eq 26 and 29. Storankin and Morachevskii[8] reported the composition, x_1, and vapor pressure, P, of the azeotrope at several temperatures. The activity coefficient of the ith component of the binary azeotropic mixture is

$$\gamma_i = P/P_i^0 \quad (37)$$

where P_i^0 is the saturated vapor pressure of the ith component at the boiling temperature of the azeotrope. Thus, the experimental values of g_{12} were obtained from combined eq 26, 29, and 37. The necessary values of P_i^0 were calculated from the Antoine equation using the data of Boublik et al.[9]

The available thermodynamic data are not sufficient for a full phenomenological analysis of the function g_{12}. As an approximation, we have assumed that (1) the functional forms for h_{12} and g_{12} are the same as those in eq 30–35 and (2) $h(T)$ at 25 °C has the value 585.9 as required by eq 36. The function $f(\phi)$ as given by eq 36 is rather asymmetrical; much smaller asymmetry was observed for the values of g_{12}. Due to the possibly large experimental error in the enthalpy values,[7] we have disregarded the form of the polynomial in eq 36 and derived another form solely from the g_{12} data. The least-squares fit to all experimental values of g_{12} together with the two above assumptions led to the following relation for g_{12}

$$g_{12} = [-0.590 + 459/T + 1.886 \times 10^5/T^2] \times [1 + 0.089(\phi_2 - \phi_1) + 0.116(\phi_2 - \phi_1)^2] \quad (38)$$

This relation reproduces all the experimental values of g_{12} with an average deviation of 1.5% (random). From the nature of the above considerations, it is obvious that the accuracy of eq 38 should not be overestimated.

Experimental Procedures and Results

Polystyrene samples with narrow distribution of molecular weight were purchased from Pressure Chemical Co., Pittsburgh, Pa. The molecular weights of these samples measured by the sedimentation equilibrium technique in benzene[10] and bromobenzene[11] solutions were reported in our previous communications. The molecular weight measured in benzene solutions was found to be 117 000 for sample 4b, 186 000 for sample 1c, 372 000 for sample 3b, and 596 000 for sample 13a. The reagent grade benzene, cyclohexane, and ethyl acetate were used for preparation of the solvent mixtures. All solvents were used without further purification. Solvent mixtures were prepared by weighing appropriate volumes of pure solvents, and the composition of solvent is reported as a volume fraction before mixing. The polystyrene solutions were prepared by dissolving a known amount of polystyrene in the solvent mixture in a volumetric flask.

The refractive indices of pure and mixed solvents were measured by a Bausch and Lomb precision refractometer using the green mercury line (546 nm). In the last column of Tables I and II are reported the values of $(dn/d\phi_1)^0$ derived from these measurements. A Brice–Phoenix differential refractometer Model BP-2000-V equipped with a special glass cell R-101-4 was used for measurements of refractive increments at constant composition of the solvent. All measurements were made using green (546 nm) and blue (436 nm) mercury lines; aqueous solutions of sodium chloride at 25 °C were used for the calibration of the differential refractometer. For each solvent mixture, the refractive increment of two polystyrene samples (4b and 3b) was measured at two different concentrations (0.01 and 0.02 g/mL). For solutions in pure cyclohexane, only sample 4b was used, since higher molecular weight samples were insoluble at 20 °C. Within our experimental

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

		$(\partial n/\partial c_3)^0_{m_2,P}$ at wavelengths		$(\partial n/\partial c_3)^0_\mu$ for sample			
ϕ_2	$\bar{v}_3$	546 nm	436 nm	4b	1c	3b	$(dn/d\phi_1)_0$
0.00	0.912	0.2180	0.2310	0.2180	0.2180	0.2176	−0.0346
0.10	0.909	0.2163	0.2289	0.2178	0.2175	0.2167	−0.0387
0.20	0.908	0.2130	0.2261	0.2145	0.2146	0.2142	−0.0422
0.30	0.907	0.2100	0.2229	0.2126	0.2121	0.2123	−0.0454
0.40	0.907	0.2062	0.2194	0.2078	0.2082	0.2087	−0.0486
0.50	0.907	0.2025	0.2159	0.2033	0.2034	0.2039	−0.0520
0.60	0.907	0.1973	0.2109	0.1950	0.1945	0.1940	−0.0560
0.70	0.908	0.1912	0.2061	0.1843	0.1861	0.1852	−0.0608
0.80	0.915	0.1836	0.1976	0.1762	0.1755	0.1749	−0.0668
0.90	0.918	0.1759	0.1888	0.1690	0.1677	0.1699	−0.0744
1.00	0.925	0.1662	0.1795	0.1660			−0.0840

precision, we have not observed any dependence of refractive increments on molecular weight or concentration. The values reported in the third and fourth column of Tables I and II represent the average values for the four solutions (each solution being measured twice).

The density measurements were made on the same polystyrene solutions using a DMA 02C digital precision density meter manufactured by A. Paar K. G., Austria. The partial specific volume of polystyrene was calculated using the expression

$$\bar{v}_3 = [1 - (\rho - \rho_s)/c_3]/\rho_s \tag{39}$$

where ρ and ρ_s are the density of solution and of the solvent mixture, respectively. Again, we have not observed any dependence of $\bar{v}_3$ on molecular weight or concentration; the values in the second column of Tables I and II are the average values (measured twice for each solution). All density and refractometric experiments were performed at 20 °C. Special care was taken to suppress as much as possible any change in solvent composition due to evaporation during the handling of the samples.

Synthetic Boundary Experiment. For measurements of refractive increments at constant chemical potential, a synthetic boundary experiment in a Spinco Model E analytical ultracentrifuge was adapted. The heavy rotor ANJ with a capillary type synthetic boundary cell and sapphire windows was used at 20 °C. For each solvent mixture, three different samples of polystyrene were measured. The cell was filled with 0.14 mL of polystyrene solution (0.003–0.005 g/mL) in one sector and 0.44 mL of appropriate solvent mixture in the other sector. The rotor was accelerated fast to complete the transport of solvent through the capillary in the shortest possible time (about 4 min). The rotor speed during the run was maintained at 5200 rpm to minimize sedimentation of polymer. At regular intervals schlieren and interference photographs of the cell were taken for about 1.5–2 h using mercury green light. The base line correction was made by removing the rotor from the chamber, shaking it without removing the cell to destroy the concentration gradient, and accelerating it again to 5200 rpm.

The present experiments with polystyrene in organic solvents were still more prone to convection inside the cell than the previously reported[1] experiments with protein in aqueous buffers. The convections are caused by mechanical disturbances, by the intermittent radiation from the heating element in the rotor chamber, and by an occurrence of a negative density gradient in some part of the cell. To combat the convections, we routinely added a small amount of the lighter solvent (cyclohexane) to the solvent sector of the cell. This excess cyclohexane created a so-called solvent boundary, which helped to stabilize the run. As the diffusion in the cell progressed, the stabilizing effect of the solvent boundary slowly disappeared. However, when this happened the polymer boundary was already spread enough to prevent convections. Of course, in experiments with single solvents this strategy could not be employed; such runs proved to be the most difficult. To prevent the disturbances of temperature, the rotor temperature was brought to about 0.5 °C below the desired temperature; both refrigeration and temperature controls were then disconnected before the start of the run. The typical rise in temperature during the run was less than 1 °C.

Evaluation of the Synthetic Boundary Experiment. The interference photographs from the ultracentrifuge are usually evaluated by means of so-called fringe count Δf, i.e., the difference in the fringe position (corrected for base line and expressed as number of fringes) for two selected points in the cell. The fringe count is related to the difference of refractive indices Δn at these two points as

$$\Delta f = h(\Delta n/\lambda_0) \tag{40}$$

where h is the thickness of the cell (1.2 cm) and λ_0 is the wavelength of the light (546 nm). The goal of the measurement is to find (for points on either side of the solvent–solution boundary) that part of Δf which corresponds to solvated polymer at the time when the boundary was formed. However, the fringe count obtained from the photographs corresponds to the superposition of the polymer boundary and solvent boundary at some later time. Due to the diffusion, the boundary spreads out and, eventually, the concentration in the cell becomes homogeneous.

For any diffusing entity, for which the diffusion constant D is independent of concentration within the range of concentration covered in the cell, the concentration profile in the cell is a unique function of the boundary conditions (length of the sector-shaped cell), initial conditions (position and size of the sharp boundary), and the product Dt, where t is the time. In our procedure, the initial position of the boundary is estimated from the schlieren photographs. The experimental concentration profile (more exactly the profile of refractive index) is sampled at three pairs of points, each of them placed more or less symmetrically around the initial boundary; the fringe count is measured for each pair and each interference photograph. Then, the diffusion of a unit-sized boundary with equivalent original position in an equivalent cell is simulated in a computer; the concentration profile is computed as a function of Dt and is sampled at the three pairs of points, which are equivalent to the experimental positions. Thus, for each pair (subscript j) a function $F_j(Dt)$ is obtained in the form of a table. The experimental fringe count Δf_j is now expressed as

$$\Delta f_j = \Delta f_p{}^0 F_j[D_p(t - \Delta t)] + \Delta f_s{}^0 F_j[D_s(t - \Delta t)] \tag{41}$$

Here, the subscript p refers to polymer boundary and s to solvent boundary; the superscript zero refers to the original sharp boundary; t is time from the start of the run; Δt is time which takes into account the period needed for the original formation of the boundary as well as the original disturbances of the boundary. A nonlinear least-squares procedure was then applied simultaneously to all three sets of the experimental values. The procedure yielded five adjustable parameters: $\Delta f_p{}^0$, $\Delta f_s{}^0$, D_p, D_s, and Δt. It was gratifying to find that the value of Δt was usually quite close to the observed time for the initial forming of the boundary. Also, D_s was usually close to the value obtained in an analogous experiment in the absence of polymer. In the actual evaluations, the value of D_s from this latter experiment was used in eq 41; we believed that the latter value yielded better precision. However, the difference in $\Delta f_p{}^0$ values calculated by the two procedures was usually insignificant. The desired values of $(\partial n/\partial c_3)^0_\mu$ were then calculated as $\Delta n/c_3$, where Δn was obtained

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

	λ for samples			L for samples			L
ϕ_2	4b	3b	13a	4b	3b	13a	smoothed
0.00							−0.28
0.10	−0.009	−0.015	−0.021	−0.11	−0.18	−0.26	−0.17
0.20	0.004	−0.005	−0.012	0.02	−0.03	−0.08	−0.05
0.30	0.019	0.041	0.029	0.10	0.21	0.15	0.10
0.40	0.065	0.057	0.061	0.30	0.26	0.28	0.29
0.50	0.129	0.143	0.118	0.57	0.63	0.52	0.55
0.60	0.162	0.147	0.135	0.74	0.67	0.61	0.66
0.70	0.112	0.132	0.098	0.59	0.69	0.51	0.61
0.80	0.097	0.063	0.079	0.66	0.43	0.54	0.52
0.90	0.034	0.059	0.037	0.41	0.71	0.45	0.46
1.00							0.41

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

	λ for samples			L for samples			L
ϕ_2	4b	1c	3b	4b	1c	3b	smoothed
0.00							−0.40
0.10	−0.036	−0.031	−0.010	−0.47	−0.38	−0.13	−0.40
0.20	−0.035	−0.037	−0.028	−0.24	−0.26	−0.19	−0.37
0.30	−0.057	−0.046	−0.050	−0.30	−0.24	−0.26	−0.32
0.40	−0.033	−0.041	−0.051	−0.15	−0.19	−0.23	−0.22
0.50	−0.015	−0.017	−0.027	−0.07	−0.08	−0.12	−0.08
0.60	0.041	0.050	0.059	0.19	0.23	0.27	0.19
0.70	0.113	0.084	0.098	0.59	0.44	0.52	0.52
0.80	0.111	0.121	0.130	0.76	0.82	0.89	0.84
0.90	0.093	0.110	0.081	1.11	1.33	0.97	1.02
1.00							1.10

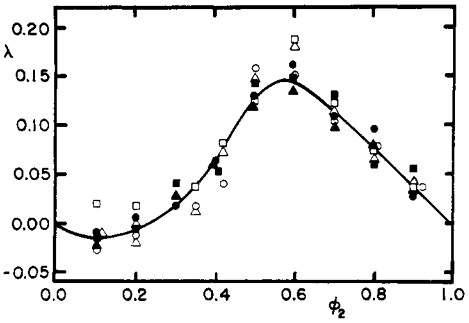


Figure 1. Coefficient of preferential adsorption λ for polystyrene in benzene (1)–cyclohexane (2) solvent mixtures as a function of solvent composition. Solid symbols show present values, and open symbols show values from sedimentation equilibrium:[2] (●, ○) sample 4b, M = 117 000; (■, □) sample 3b, M = 372 000; (▲) sample 13a, M = 596 000; (△) sample 7b, M = 35 600.

from eq 40 with $\Delta f_p{}^0$ values and c_3 was the concentration known from the sample preparation. The values of $(\partial n/\partial c_3)_\mu^0$ are collected in the fifth-to-seventh columns of Tables I and II.

Discussion

For two-component systems, the refractive increments measured by a refractometer and by means of the synthetic boundary experiment should be the same. It is obvious from Tables I and II that this was indeed the case for polystyrene solutions in all three simple solvents. Similarly, good agreement was observed for the refractive increment of sodium chloride in water measured by the two techniques. Thus, the synthetic boundary experiment is seen to yield correct and rather precise values.

Using eq 13 and 21, the values of λ and L were calculated; they are reported in Tables III and IV and in Figure 1–4. The value of λ is calculated as a small difference of two close quantities: all the experimental errors are magnified in these values. Nevertheless, the data define reasonably smooth curves in Figures 1–4. We have not observed any clear-cut dependence of our data on molecular weight within our experimental error; we are interpreting them therefore as independent of molecular

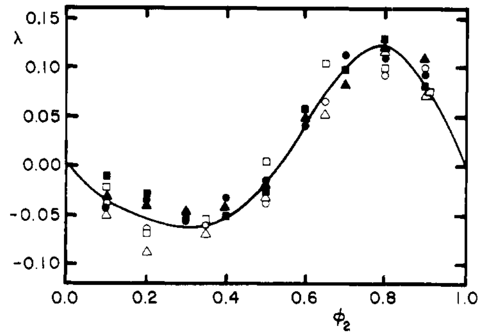


Figure 2. Coefficient of preferential adsorption λ for polystyrene in ethyl acetate (1)–cyclohexane (2) solvent mixtures as a function of solvent composition. Solid and open symbols have the same meaning as in Figure 1: (●, ○) sample 4b, M = 117 000; (■, □) sample 3b, M = 372 000; (▲) sample 1c, M = 186 000; (△) sample 7b, M = 35 600.

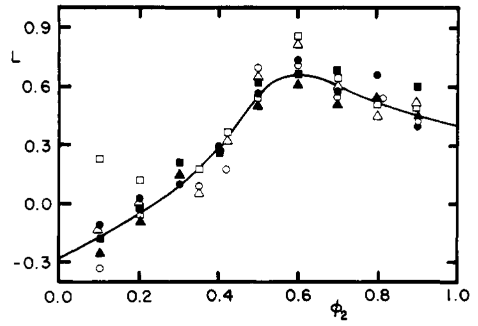


Figure 3. Parameter L for polystyrene in benzene (1)–cyclohexane (2) solvent mixtures. The symbols have the same meanings as those in Figure 1.

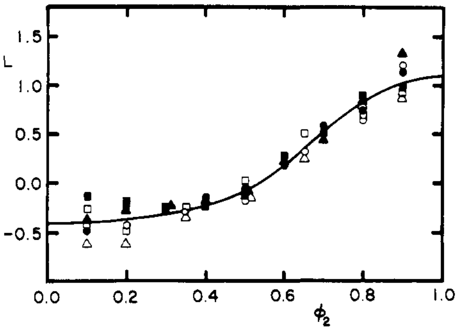


Figure 4. Parameter L for polystyrene in ethyl acetate (1)-cyclohexane (2) solvent mixtures. The symbols have the same meanings as those in Figure 2.

weight. Included in Figures 1-4 are also the values of λ and L, which were obtained in our previous study[2] for the same experimental system by an entirely different method: combination of densitometry with sedimentation equilibria. While the present data may exhibit slightly smaller scatter than the previous ones, the agreement between the two sets is very good. Actually, the lines, which were drawn through the data, as well as the following analysis, are based on simultaneous interpretation of both sets of data.

It is obvious from Figures 1-4 that both of our experimental systems exhibit an inversion of the preferential adsorption. Cyclohexane is preferentially adsorbed onto polystyrene when its volume fraction is less than about 0.52 in the cyclohexane-ethyl acetate solvent mixture, or less than about 0.23 in the cyclohexane-benzene mixture. Thus, the inversion seems to be a rather common phenomenon, which persists even in mixtures of good solvents with marginal ones.

Carrying our analysis further, we have evaluated the value of ($g_{13}^0 - lg_{23}^0$) and the function $g_T^0(\phi_1)$ from eq 18, 20, and 23. The integrals were computed numerically using the smoothed values of L (reported in Tables III and IV). For g_{12} we have used eq 35 and 38, which at 20 °C read as

$$g_{12} = 0.505[1 + 0.038(\phi_2 - \phi_1) + 0.030(\phi_2 - \phi_1)^2] \quad (42)$$

for benzene (1)-cyclohexane (2) and

$$g_{12} = 1.197[1 + 0.089(\phi_2 - \phi_1) + 0.116(\phi_2 - \phi_1)^2] \quad (43)$$

for ethyl acetate (1)-cyclohexane (2). The value of ($g_{13}^0 - lg_{23}^0$) is -0.049 for polystyrene (3) in benzene (1)-cyclohexane (2) and 0.0003 for polystyrene (3) in ethyl acetate (1)-cyclohexane (2). Both of these values are rather small. The calculated ternary function g_T^0 is presented in Figures 5 and 6. For benzene-cyclohexane mixtures, g_T^0 is very small for mixtures with large amounts of the better solvent benzene; it increases with increasing concentration of cyclohexane. In the mixtures of ethyl acetate and cyclohexane (two marginal solvents), the function is rather high at all compositions of the mixed solvent. At the present time, we are not attaching much significance to the details of these curves: they are too strongly influenced by the form of the relations employed for g_{12} and by the shape of the somehow arbitrarily smoothed function L.

To complete the analysis, we have repeated the calculation of $\chi_T^0(\phi_1)$ from eq 19 as in our previous study[2] using the values of χ_{i3}^0 and A_2 as reported there. However, for g_{12}, g_T^0, L, and b_{22}, we have employed the functions derived in the present article. The resulting data are plotted in Figures 5 and 6. While there seems to be some dependence on molecular weight, especially for polystyrene in ethyl acetate-cyclohexane, we feel that the differences are within experimental error, and we interpret the dependences of χ_T^0 on solvent composition by a single line. Again, the character of these functions appears to be different for a mixture of two marginal solvents and for a mixture of a good solvent with a poor one.

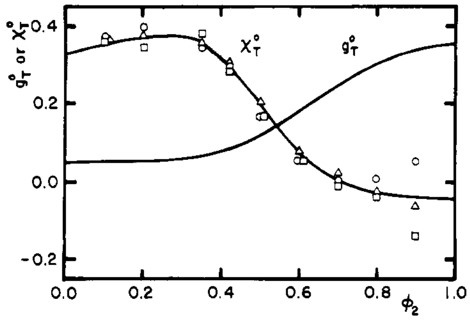


Figure 5. Polystyrene in mixtures of benzene (1) and cyclohexane (2). Parameter g_T^0 as a function of solvent composition when g_{12} is given by eq 42; experimental points represent parameter χ_T^0. The symbols have the same meanings as those in Figure 1.

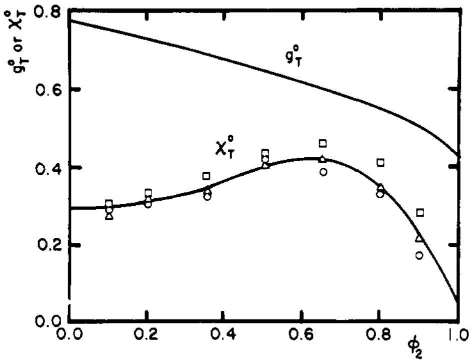


Figure 6. Polystyrene in mixtures of ethyl acetate (1)-cyclohexane (2). Parameter g_T^0 as a function of solvent composition when g_{12} is given by eq 43. Experimental points represent parameter χ_T^0. The symbols have the same meanings as those in Figure 2.

There is a significant difference between the presently reported functions g_T^0 and χ_T^0 and the functions presented in our previous paper.[2] Part of the difference results from the present use of more extensive and more precise experimental data for the preferential adsorption. However, the main source of the difference is the function g_{12}: in the previous study some rather tentative relations were employed for it. The present functions g_T^0 and χ_T^0 are based on experimental expressions for g_{12} and, consequently, should be considered as more representative.

Conclusions

The present measurement of preferential adsorption onto polystyrene in two mixed solvent systems, which was based on the measurements of refractive increments, yielded values which agreed well with previous results, which were based on the measurements of partial specific volumes.[2] The present method is experimentally less demanding and yields values which exhibit somewhat smaller experimental scatter. The inversion of the preferential adsorption was confirmed both for a mixture of two marginal solvents and for a mixture of a marginal solvent with a good one.

To allow a meaningful thermodynamic analysis of our three-component systems, the binary data for our mixed solvents were analyzed carefully, and semiempirical relations were developed for the binary interaction coefficient g_{12} as a function of temperature and of solvent composition. These relations were used for calculation of the semiempirical functions g_T^0 and χ_T^0. These latter functions have rather sizable values which provide the justification for the introduction of the ternary term into the phenomenological description of the ternary system (eq 14). The character of these functions seems to be different for a mixture of two marginal solvents and for a mixture of a poor solvent with a good one. However, measurements on a larger number of ternary systems are needed before any conclusion about these trends can be drawn.

Acknowledgment. The authors are grateful to the Robert A. Welch Foundation (Grant No. F-563) for financial support of this study.

References and Notes

(1) P. Munk, R. G. Allen, and M. E. Halbrook, *J. Polym. Sci., Polym. Symp.*, **42**, 1013 (1973).
(2) S. G. Chu and P. Munk, *Macromolecules*, **11**, 879 (1978).
(3) C. Strazielle in "Light Scattering from Polymer Solutions", M. B. Huglin, Ed., Academic Press, New York, 1972.
(4) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939).
(5) K. C. Chao and O. A. Hougen, *Chem. Eng. Sci.*, **7**, 246 (1958).
(6) K. Elliott and C. J. Wormald, *J. Chem. Thermodyn.*, **8**, 881 (1976).
(7) J. P. E. Grolier and A. Villard, International DATA Series, A, edited by Texas A&M University, College Station, Texas, 1973, p 111.
(8) A. V. Storonkin and A. G. Morachevskii, *Zh. Fiz. Khim.*, **31**, 42 (1957).
(9) T. Boublik, V. Fried, and E. Hala, "The Vapor Pressures of Pure Substances", Elsevier, New York, 1973.
(10) S. G. Chu and P. Munk, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1163 (1977).
(11) S. G. Chu and P. Munk, *Macromolecules*, **11**, 101 (1978).

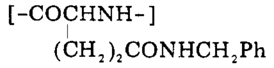
Preferential and Absolute Adsorption by Poly[N^5-(2-hydroxyethyl)-L-glutamine-*co*-N^5-benzyl-L-glutamine] in Water/2-Chloroethanol Mixtures[1]

Claude Feyereisen, Michel Morcellet, and Claude Loucheux*

Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques de Lille, 59650 Villeneuve D'ASCQ, France. *Received July 17, 1978*

ABSTRACT: The synthesis and characterization of water-soluble random poly[N^5-(2-hydroxyethyl)-L-glutamine-*co*-N^5-benzyl-L-glutamine] and their conformational properties in water and in mixed water/organic solvents are described. Preferential adsorption by the copolymers in water/2-chloroethanol mixtures was determined by the density increment technique. Preferential adsorption by 2-chloroethanol is dependent on copolymer composition. The magnitude of preferential and absolute adsorption increases when the copolymers are enriched in nonpolar monomeric units. The preferential interaction results are also discussed in relation to the solvent-induced coil-to-helix conformational transition. The results are interpreted in terms of hydrophobic interactions.

Preferential and absolute adsorptions by proteins in mixed water/organic solvent systems have been studied in relation to a possible conformational transition.[2-6] In the case of the water/2-chloroethanol solvent system, it was assumed[3-6] that unfolding of globular proteins was accompanied by an increase of preferential and absolute adsorption of 2-chloroethanol by the nonpolar residues buried in the "hydrophobic pocket", which are brought in contact with the solvent during the denaturation of the conformation in water. Timasheff and co-workers[3-6] postulated that the helicogenic power of an organic solvent is related to its ability to interact with hydrophobic residues in globular proteins, thus destroying the native conformation. The study of synthetic polypeptides showed that the helicogenic power of dioxane for aqueous ionized poly(α-L-glutamic acid) is related to adsorption of dioxane by the polymer.[7] The binding of dioxane to the dissociated carboxyl end group weakens electrostatic repulsions, thus allowing a coil-to-helix transition. The study of another polyelectrolyte, poly(L-Lys·HBr), in various water/organic solvent systems, showed[8] that preferential adsorption of the organic solvent is dependent on the nature of the solvent system, but no relation could be found between the variations of preferential interactions and the properties of the organic solvents. The study of a series of nonionizable polypeptides, poly[N^5-(2-hydroxyethyl)-L-glutamine] (PHEG) and poly[N^5-(3-hydroxypropyl)-L-glutamine], in water/2-chloroethanol mixtures emphasized that preferential adsorption of 2-chloroethanol is dependent on the hydrophobic character of the polypeptide and is closely related to the solvent-induced coil-to-helix transition.[9,10] These findings led us to undertake the synthesis of copolymers of variable hydrophobic nature to look for a possible correlation between the interactions of 2-chloroethanol with the copolymers and their hydrophobic character. N^5-(2-Hydroxyethyl)-L-glutamine (HEG) was chosen as one of the monomeric residues, because of its hydrophilic character.[11] In order to counterbalance the effects of the hydrophilic residue, a hydrophobic residue was introduced by statistical substitution of a phenyl group for the hydroxymethyl end group of HEG, which was expected to lead to marked hydrophobic interactions, as was observed for copolymers of L-glutamic acid, with γ-benzyl L-glutamate,[12] and copolymers of L-glutamic acid, with 2-nitro-γ-benzyl L-glutamate.[13] The hydrophobic N^5-benzyl-L-glutamine (BGln) residue was synthesized by


$$[\text{-CO}\underset{\substack{|\\ (\text{CH}_2)_2\text{CONHCH}_2\text{Ph}}}{\text{C}}\text{HNH-}]$$

aminolysis of the γ-benzyl L-glutamate side chain of poly(γ-benzyl L-glutamate) (PBLG) with benzylamine (see Experimental Section). Preferential adsorption can be determined by light scattering,[2-4] differential refractometry,[3,4,7,8] or density increments[9,14,15] measurements. For the water/2-chloroethanol mixtures, it is convenient to use

0024-9297/79/2212-0613$01.00/0