A Sedimentation Equilibrium Study of Thermodynamic Properties of Polystyrene in Bromobenzene

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ABSTRACT: A method of analysis of sedimentation equilibrium data was developed for nonideal, slightly polydisperse, polymer solutions. The method was designed to yield the interaction factors χ and F as a function of concentration. It yielded also the molecular weight and the polydispersity parameter $u = \overline{M}_z/\overline{M}_w - 1$. The method was used to obtain the interaction parameters for six samples of polystyrene in bromobenzene in a concentration range up to 7 vol %. The interaction parameters for samples with different molecular weight do not converge to a common value as required by existing theories of concentrated solutions. The necessity of modifying the current theories is indicated.

In a recent paper[1] we used the sedimentation equilibrium method for a study of the thermodynamic behavior of polystyrene in benzene, a good solvent. We were especially interested in verification of Koningsveld et al. theory[2] of the dependence of the polymer–solvent interaction term on the concentration and on molecular weight of the polymer. We were not able to arrive at a definitive conclusion because our experimental data did not cover a sufficiently broad range of concentrations. The concentration range was limited by the interference optics in the ultracentrifuge, which cannot handle gradients of refractive index beyond some critical value. In the present study we employed another good solvent, bromobenzene. The refractive increment of polystyrene in bromobenzene is low enough to permit measurements up to concentrations of over 7 vol %. In the previous study,[1] we assumed during the thermodynamic analysis that our narrow polymer fractions were monodisperse. Presently, we also analyze the effect of polydispersity on the evaluation of the thermodynamic data from sedimentation equilibrium measurements.

Theoretical

We will consider a polydisperse polymer in a single-component solvent. We will use three composition variables: number of moles n, concentration (g/mL) c, and volume fraction ϕ. In our notation the subscript s denotes solvent, i or k denote individual polymer components, and j denotes all components including solvent. Subscript p is used for composition variables and means the sum over all polymer components, e.g., $c_p \equiv \Sigma_i c_i$. Molar volumes are designated as V_j with $\sigma_j \equiv V_j/V_s$ and molecular weights as M_j; R is the universal gas constant, T the absolute temperature, and P the pressure. The molecular weight averages $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ are defined in a standard way as

$$\overline{M}_n \equiv \sum_i c_i \Big/ \sum_i (c_i/M_i) \tag{1a}$$

$$\overline{M}_w \equiv \sum_i c_i M_i \Big/ \sum_i c_i \tag{1b}$$

$$\overline{M}_z \equiv \sum_i c_i M_i^2 \Big/ \sum_i c_i M_i \tag{1c}$$

The polydispersity index u is defined as

$$u \equiv \overline{M}_z/\overline{M}_w - 1 \tag{2}$$

For simplicity, we will neglect any excess volume of mixing. The specific volume v will be the same for all polymer species. Then, the following relations apply.

$$\phi_i = c_i v \tag{3a}$$

$$\phi_j = n_j V_j/(n_s V_s + \sum_i n_i V_i) \tag{3b}$$

$$V_i = M_i v \tag{3c}$$

The buoyancy factor $(1 - v\rho)$ reads under these circumstances

$$(1 - v\rho) = (1 - v\rho_s)\phi_s \tag{4}$$

where ρ is the density of the solution and ρ_s is the density of the solvent.

The free enthalpy (Gibbs free energy) of mixing ΔG_{mix} can be quite generally written in a form similar to the well-known Flory–Huggins expression[3] as

$$\Delta G_{mix}/RT = n_s \ln \phi_s + \sum_i n_i \ln \phi_i + n_s \phi_p g \tag{5}$$

This relation is actually a definition of the excess free enthalpy function g. The function g is a complicated function of the polymer concentration ϕ_p, of the average molecular weight of the polymer, and of the whole distribution function of molecular weights. To simplify the following calculations, we will assume that, for a given polymer sample, g is a function only of ϕ_p and is not influenced by possible redistribution of molecular weights along the column in sedimentation equilibrium experiments. Such an approximation is possible because g is not inordinately sensitive to changes in molecular weight, especially in the region of more concentrated solutions. The approximation gets better as the distribution of molecular weights gets narrower.

The chemical potential differences $\Delta\mu_j$ can be obtained easily by differentiating ΔG_{mix} as

$$\Delta\mu_s/RT = \ln \phi_s + \phi_p - \sum_i (\phi_i/\sigma_i) + \phi_p^2 \chi \tag{6}$$

$$\Delta\mu_i/RT = \ln \phi_i + 1 - \sigma_i[\phi_s + \sum_k (\phi_k/\sigma_k)] + \sigma_i \phi_s^2 X \tag{7}$$

$$\chi \equiv g - \phi_s(\partial g/\partial \phi_p)_{P,T} \tag{8}$$

$$X \equiv g + \phi_p(\partial g/\partial \phi_p)_{P,T} \tag{9}$$

It is usual to expand the function χ into series as

$$\chi = \chi_0 + \chi_1 \phi_p + \chi_2 \phi_p^2 + \ldots \tag{10}$$

Realizing that $\Sigma_i(\phi_i/\sigma_i) = c_p V_s/\overline{M}_n$ and expanding $\ln \phi_s$ and χ into series, we may rearrange eq 6 into a form

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$$\begin{aligned}-\Delta\mu_s/c_pRTV_s &= 1/\overline{M}_n + (\upsilon^2/V_s)(\tfrac{1}{2} - \chi_0)c_p \\ &\quad + (\upsilon^3/V_s)(\tfrac{1}{3} - \chi_1)c_p^2 + \ldots \\ &= 1/\overline{M}_n + A_2c_p + A_3c_p^2 + \ldots \end{aligned} \qquad (11)$$

which represents the virial expansion of chemical potential of the solvent and relates the virial coefficients A_2 and A_3 with the coefficients χ_0 and χ_1.

The derivative $(\partial\mu_i/\partial c_k)_{P,T}$, which is needed for sedimentation equilibrium, is easily obtained from eq 7 as

$$(\partial\mu_i/\partial c_k)_{P,T} = RT[\delta_{ik}/c_i + \sigma_i\upsilon(1 - 1/\sigma_k) - 2F\phi_s\sigma_i\upsilon] \qquad (12)$$

$$F \equiv \chi + (\phi_p/2)(\partial\chi/\partial\phi_p)_{P,T} \equiv X - (\phi_s/2)(\partial X/\partial\phi_p)_{P,T} \qquad (13)$$

$$F = \chi_0 + (3/2)\chi_1\phi_p + \ldots \qquad (13a)$$

Here, $\delta_{ik} = 1$ for $i = k$ and $\delta_{ik} = 0$ for $i \neq k$.

Our goal is to evaluate function F from sedimentation equilibrium experiments. The condition for equilibrium in an ultracentrifuge for each component of the solute is

$$M_i(1 - \upsilon\rho)\omega^2r = \sum_k(\partial\mu_i/\partial c_k)_{P,T}(dc_k/dr) \qquad (14)$$

where ω is the angular velocity of rotor and r is the distance from rotor axis.

When eq 4 and 12 are substituted into eq 14, σ's are expressed through M's and summation over k is performed using eq 1, we obtain for each component

$$\begin{aligned}M_i(1 - \upsilon\rho_s)\omega^2r\phi_s = RT\{&(1/c_i)(dc_i/dr) \\ &+ M_i(dc_p/dr)[(\upsilon^2/V_s)(1 - 2F\phi_s) - \upsilon/\overline{M}_n] \\ &+ M_i(c_p\upsilon/\overline{M}_n^2)(d\overline{M}_n/dr)\}\end{aligned} \qquad (15)$$

In this and following relations, the molecular weight averages are functions of the position in the cell and, consequently, for a given equilibrium experiment they are unique functions of the total concentration c_p. Realizing that $d\overline{M}_n/dr = (d\overline{M}_n/dc_p)(dc_p/dr)$ we may transform eq 15 into a convenient form

$$c_iM_iB = dc_i/dr \qquad (16)$$

$$\begin{aligned}B \equiv\ &(1 - \upsilon\rho_s)\omega^2r\phi_s/RT \\ &+ (dc_p/dr)[(\upsilon/\overline{M}_n)(1 - d\ln\overline{M}_n/d\ln c_p) \\ &- (\upsilon^2/V_s)(1 - 2F\phi_s)]\end{aligned} \qquad (17)$$

The expression B is common for all components of the solute. Summation of both sides of eq 16 over all polymer species yields after slight rearrangement

$$B = (dc_p/dr)/c_p\overline{M}_w \qquad (18)$$

Multiplication of eq 16 by M_i and summation yields

$$B = (dc_p/dr)(1 + d\ln\overline{M}_w/d\ln c_p)/c_p\overline{M}_z \qquad (19)$$

Similarly, division of eq 16 by M_i and summation yields

$$B = (dc_p/dr)(1 - d\ln\overline{M}_n/d\ln c_p)/c_p\overline{M}_n \qquad (20)$$

Comparison of eq 18–20 leads to expressions

$$d\ln\overline{M}_n/d\ln c_p = 1 - (\overline{M}_n/\overline{M}_w) \qquad (21)$$

$$d\ln\overline{M}_w/d\ln c_p = (\overline{M}_z/\overline{M}_w) - 1 = u \qquad (22)$$

Thus, the variation of the average molecular weight with the concentration in the sedimentation cell depends only on the local polydispersity and not at all on the interaction function g or χ or F (at least as long as the function g does not depend on the distribution function of molecular weights).

Combination of eq 17, 18, and 21 yields after some manipulation the expression for F as

$$F = \frac{1}{2}\left\{\frac{1}{\phi_s} - \left[\frac{(1 - \upsilon\rho_s)\omega^2r}{RT(dc_p/dr)} - \frac{1}{c_p\overline{M}_w}\right]\frac{V_s}{\upsilon^2}\right\} \qquad (23)$$

In our previous paper,[1] we have derived a special case of eq 23 with the molecular weight of a monodisperse polymer M_m replacing the position dependent average $\overline{M}_w$.

In eq 23 F, which is a function of concentration and, consequently, of the position in the cell, is expressed as a function of experimentally accessible quantities and of the position-dependent value $\overline{M}_w$. For evaluation of F we need to know $\overline{M}_w$ as a function of the position in the cell. However, in the region of high concentrations and high molecular weights, the contribution of the term $1/c_p\overline{M}_w$ to the value of F is very small. For example, for a typical polymer–solvent system and for $c_p = 0.05$ g/mL, $\overline{M}_w = 10^6$, the contribution to F is about 0.001, i.e., it is comparable with overall experimental error. Consequently, in this experimental region almost any estimate of $\overline{M}_w$ would be good enough. Even in the moderate concentration region, i.e., above 0.01 g/mL (all molecular weights), it is easy to arrive at reasonable estimates of $1/c_p\overline{M}_w$. However, for the lowest concentrations more elaborate techniques are needed. We will describe one of them in the latter part of this study.

Experimental Section

Polystyrene samples with narrow distribution of molecular weights were obtained from Pressure Co., Pittsburgh, Pa.; the same samples were used in our previous studies.[1,4,5] Reagent grade bromobenzene was used as a solvent without further purification; its density was 1.4944 g/mL. Partial specific volume of polystyrene in bromobenzene at 20 °C was measured by A. Paar Precision Density Meter DMA 02C; its value was 0.924 mL/g.

The concentration differences Δc_p between two points in the ultracentrifuge cell are measured by means of the interference optics and are expressed as a fringe count Δf, which is related to Δc_p as

$$\Delta f = h(\Delta n/\lambda) = (h/\lambda)(\Delta n/c_p)\Delta c_p = K\Delta c_p \qquad (24)$$

Here, h is the thickness of the liquid column in the cell (1.2 cm), λ is the wavelength of the light under vacuum (5460 Å), and $(\Delta n/c_p)$ is the refractive index increment of the solute. $(\Delta n/c_p)$ was measured by Brice-Phoenix Differential Refractometer Model BP-2000V equipped with a special glass cell R-101-4. For polystyrene in bromobenzene at 5460 Å and 20 °C, $(\Delta n/c_p)$ was found to be independent of the concentration at least up to $c_p = 0.062$ g/mL. It is equal to 0.0467 mL/g; that corresponds to $K = 1033$ fringe/(g/mL).

Intrinsic viscosity was measured at 20 °C in bromobenzene by an automatic viscometer Fica Viscomatic.

The sedimentation equilibrium experiments were performed at 20 °C in a Spinco Model E ultracentrifuge equipped with an electronic speed control, titanium ANH rotor, Kel F coated aluminum double sector centerpiece, sapphire windows, and schlieren and interference optics. The interference photographs were evaluated using a Fourier transform algorithm[6] as described by Munk and Halbrook.[4] The basic analysis of the raw data was essentially the same as in ref 4 with few modifications.

Polystyrene is less dense than bromobenzene; it was therefore floating instead of sedimenting. That led to some trivial changes in the evaluation procedure. For all experiments we adjusted the conditions to make the concentration of polystyrene at the bottom essentially zero. We estimated the residual concentration c_b at the bottom assuming that the concentration is an exponential function of the square of the radius in the lowest concentration region. For most experiments c_b was less than 0.02 fringes; only for the runs with lowest molecular weight sample did c_b reach a value of 0.08 fringes, which is still very low.

For each sample of polystyrene at least two equilibrium runs were performed: a long column experiment designed to obtain the thermodynamic data in as broad a region of concentrations as possible, and at least one short column experiment for obtaining the basic information about the whole sample. In the long column experiments 0.40 mL (~12-mm column) of solution was used with an original concentration of 0.03 g/mL. After overspeeding the run for 1 day at 20 000 rpm, the final speed of the rotor was adjusted to produce the interference fringes as steep as possible while still being visible. The final speed ranged from 13 000 rpm for the high molecular weight samples to 18 000 rpm for the lowest M. The concentration pattern

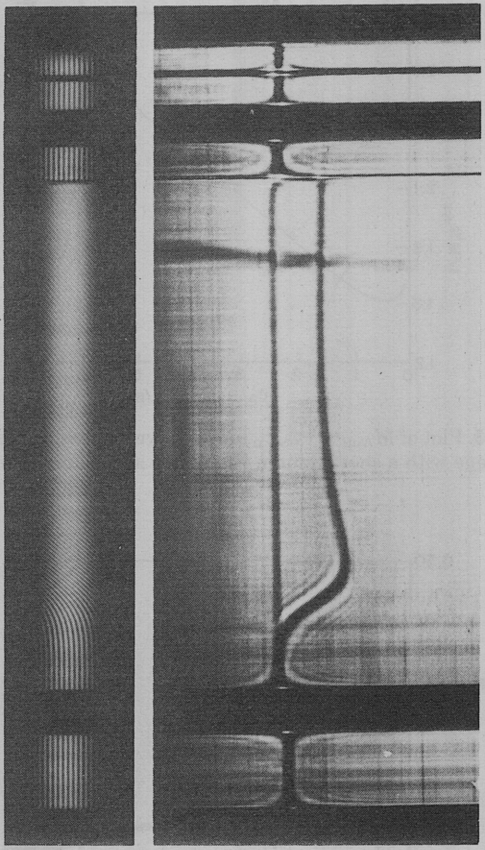

Figure 1. Interference and schlieren photographs of a sedimentation equilibrium run with a long column. Polystyrene in bromobenzene, sample **1c**, 13 000 rpm, after 14 days.

(Figure 1) was similar to that observed for polystyrene in benzene in our previous study[1] as well as to the pattern for polystyrene in toluene reported by Scholte;[7] the concentration gradient reached a maximum at some moderate concentration and then gradually decreased in the region of high concentrations. The run was terminated when no difference could be detected on the interference patterns photographed at successive days; 14–17 days were needed. The cell was then rinsed and refilled with solvent without disassembling it for baseline correction run. In the short column experiments the original concentration was 0.005 g/mL; 0.15 mL (~4.5-mm column) of solution was used.

Results

It is convenient[4] to define a quantity M_{App}, which may be expressed from relation 23 as

$$\frac{1}{M_{\mathrm{App}}} \equiv \frac{(1-\upsilon\rho_{\mathrm{s}})\omega^2 r c_{\mathrm{p}}}{RT(\mathrm{d}c_{\mathrm{p}}/\mathrm{d}r)} = \frac{1}{\overline{M}_{\mathrm{w}}} + c_{\mathrm{p}}\left(\frac{1}{\phi_{\mathrm{s}}} - 2F\right)\frac{\upsilon^2}{V_{\mathrm{s}}} \quad (25)$$

For the analysis of the experimental data on dilute polymer solutions, the usefulness of the square-root plots has been frequently[1,3,4] demonstrated. For monodisperse polymers with molecular weight M_{m}, the plot of $M_{\mathrm{App}}^{-1/2}$ vs. c_{p} is approximately linear over an appreciable interval of concentrations. The intercept i and slope s of a tangent to this dependence can be represented by approximate relations

$$i \doteq M_{\mathrm{m}}^{1/2}[1 + \tfrac{1}{2}(A_2^2 - 3A_3/M_{\mathrm{m}})M_{\mathrm{m}}^2 c_{\mathrm{p}}^2 + \ldots] \quad (26)$$

$$s \doteq M_{\mathrm{m}}^{1/2}[A_2 - (A_2^2 - 3A_3/M_{\mathrm{m}})M_{\mathrm{m}} c_{\mathrm{p}} + \ldots] \quad (27)$$

$$is \doteq A_2 - (A_2^2 - 3A_3/M_{\mathrm{m}})M_{\mathrm{m}} c_{\mathrm{p}} + \ldots \quad (28)$$

During the derivation of eq 26–28, F was developed into series as in eq 13a and virial coefficients A_2 and A_3 introduced as defined in eq 11. In eq 26–28 c_{p} represents the concentration at the point where the tangent was drawn. It is usual[8,9] to write the relation between second and third virial coefficients as

$$A_3 = \gamma A_2^2 M_{\mathrm{m}} \quad (29)$$

The coefficient γ is found to be slightly less than ⅓; the plot of $M_{\mathrm{App}}^{-1/2}$ vs. c_{p} is slightly curved down, but the deviation from linearity can be usually observed only for values of $M_{\mathrm{App}}^{-1/2}$, which are at least 2.0 to 2.5 times higher than i. Thus, if the sedimentation equilibrium experiment is performed under conditions when the whole dependence is under this limit, the dependence is linear, the higher terms in eq 26–28 are completely negligible, and M_{m} and A_2 may be easily obtained from i^2 or is, respectively. As a first approximation, we have evaluated our short column sedimentation equilibrium experiments using expressions 26 and 28, which are valid for monodisperse samples. [For the highest molecular weight sample **14b**, the correction term in eq 26 was significant. For this sample we obtained the molecular weight from experiments in ethyl acetate, a much poorer solvent (see ref 1).] The value of A_2 obtained in this way yielded the approximate value of χ_0 (of eq 11). The value of molecular weight was then used as $\overline{M}_{\mathrm{w}}$ for calculation of F according to eq 23. This was the same procedure as used in our previous communication.[1] The values of F obtained using this approximation were identical within 0.001 with the values calculated as a second approximation (described below) for concentrations higher than $\phi_{\mathrm{p}} = 0.004$ in short column experiments and $\phi_{\mathrm{p}} = 0.01$ for long column ones. Only for the lowest molecular weight sample **7b** did the deviation reach 0.003.

In our second approximation, we assume that (i) the local polydispersity parameter u is a characteristic of the sample and is not influenced by the redistribution of the sample in the cell (similar assumption has been made by Scholte[7]) and (ii) the local value of F for a given sample depends only on the local concentration but not on local average molecular weight or local distribution of molecular weights. Under these assumptions, the local value of $\overline{M}_{\mathrm{w}}$ can be obtained by integration of eq 22 as

$$\overline{M}_{\mathrm{w}} = \overline{M}_{\mathrm{w,tot}} c_{\mathrm{p}}^{u} \textstyle\int c_{\mathrm{p}}\, \mathrm{d}V / \int c_{\mathrm{p}}^{u+1}\, \mathrm{d}V \quad (30)$$

where $\overline{M}_{\mathrm{w,tot}}$ is the value of $\overline{M}_{\mathrm{w}}$ for the whole sample. The integrals are taken over all volume elements of the solution column $\mathrm{d}V$. The volume element is proportional to $r\,\mathrm{d}r$ for sector-shape centerpieces; for rectangular centerpieces it is proportional to $\mathrm{d}r$. At a particular point in the cell with concentration c_{p}^*, the local weight average molecular weight is equal to the average for the whole sample. Using eq 30 we may calculate c_{p}^* as

$$(c_{\mathrm{p}}^*)^u = \textstyle\int c_{\mathrm{p}}^{u+1}\, \mathrm{d}V / \int c_{\mathrm{p}}\, \mathrm{d}V \quad (31)$$

For all our experiments, c_{p}^* corresponded to 45–70% of the maximum concentration in the cell (i.e., at meniscus).

For the second approximation, the values of $\overline{M}_{\mathrm{w,tot}}$ and u are needed. One relation for them was again obtained from the plot of $M_{\mathrm{App}}^{-1/2}$ vs. c_{p}. For polydisperse polymers, the intercept and slope can be expressed by the following relations

$$i \doteq \frac{2+u}{2\overline{M}_{\mathrm{w}}^{1/2}}\left\{1 - A_2\left(\frac{u}{2+u}\right)\overline{M}_{\mathrm{w}} c_{\mathrm{p}} + \tfrac{1}{2}[A_2^2(1+2u) - 3A_3/\overline{M}_{\mathrm{w}}]\overline{M}_{\mathrm{w}}^2 c_{\mathrm{p}}^2 + \ldots\right\} \quad (32)$$

$$i^2 \doteq \frac{(2+u)^2}{4\overline{M}_{\mathrm{w}}}\left\{1 - A_2\left(\frac{2u}{2+u}\right)\overline{M}_{\mathrm{w}} c_{\mathrm{p}} + \left[A_2^2\left(1 + 2u + \frac{u^2}{(2+u)^2}\right) - 3A_3/\overline{M}_{\mathrm{w}}\right]\overline{M}_{\mathrm{w}}^2 c_{\mathrm{p}}^2 + \ldots\right\} \quad (33)$$

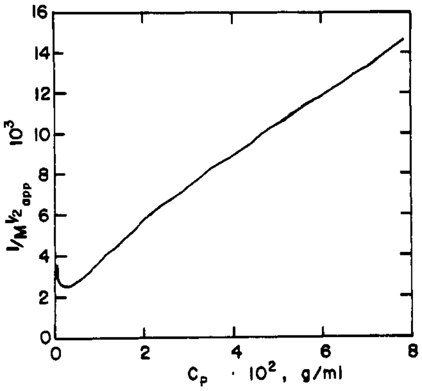

Figure 2. Plot of $M_{App}^{-1/2}$ vs. c_p for polystyrene sample **13a** in bromobenzene with a long column run. The line connects the experimental points, which were smoothed locally to eliminate photographic noise; long range smoothing was not employed.

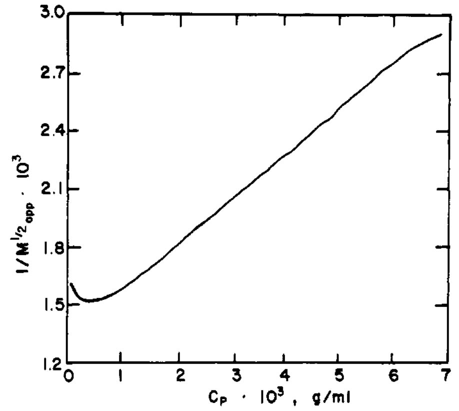

Figure 3. Plot of $M_{App}^{-1/2}$ vs. c_p for polystyrene sample **13a** in bromobenzene with a short column run. Same smoothing as in Figure 2.

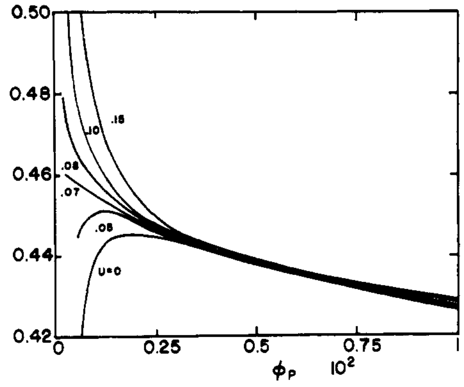

Figure 4. Plot of parameter F vs. ϕ_p for several values of u. Polystyrene sample **3b** in bromobenzene with a short column run.

$$s \doteq \frac{u}{2c_p\overline{M}_w^{1/2}} + \overline{M}_w^{1/2}\left\{A_2\left(\frac{2+u}{2}\right) - \left[A_2^2\left(\frac{4+3u}{4}\right) - \frac{3A_3}{\overline{M}_w}\left(\frac{4+u}{4}\right)\right]\overline{M}_w c_p + \ldots\right\} \quad (34)$$

$$is \doteq -\frac{u^2+2u}{4c_p\overline{M}_w} + A_2[1+u+u^2/2] - \left[A_2^2 - \frac{3A_3}{\overline{M}_w}\frac{(u+2)^2}{4}\right]\overline{M}_w c_p + \ldots \quad (35)$$

These relations obviously reduce to eq 26–28 for monodisperse polymers with $u = 0$. The right-most terms in eq 32–35 are important at high concentrations only, similarly as the corresponding terms in eq 26–28. They may be neglected if the maximum concentration in the cell is low enough; that was the case with most of our short column experiments.

The first term in eq 34 and 35 is inversely proportional to the polymer concentration; the $M_{App}^{-1/2}$ vs. c_p curves exhibit a hyperbolic upturn in the region of lowest concentrations. The significance of this upturn increases with increasing value of the polydispersity parameter u. Typical examples are shown in Figures 2 and 3 for sample **13a** which has relatively high molecular weight and more pronounced polydispersity. In the long column experiment (Figure 2) the upturn at low concentrations is very prominent as well as the down curvature at high concentrations, which is due to value of $\gamma < 1/3$. However, for the short column experiment (Figure 3) the dependence is sensitively linear over a broad range of concentrations emcompassing the characteristic concentration c_p^*. The intercept of this linear portion i_{lin} was assumed to represent (eq 32) the quantity $(2 + u)/2\overline{M}_{w,tot}^{1/2}$. Function F was then calculated from eq 23 using eq 30, the value of i_{lin}, and several values of u. When a too low value of u was used, F exhibited a sharp hyperbolic downward curvature in the region of very low concentrations; a too high value produced sharp upward curvature (Figure 4). The requirement that the dependence F vs. c_p did not change its character down to lowest concentrations proved to be a rather sensitive test for the selection of u and for the final calculation of F. Of course, the method yields some range of acceptable values of u and the values of F cannot be relied upon down to lowest concentration. However, after extensive analysis we consider our F values dependable down to the concentration $c_p = 0.001$ g/mL. Our value of $F_0 = \chi_0$ was deduced from the product $is \doteq A_2$ of the linear portion of the plot $M_{App}^{-1/2}$ vs. c_p (as discussed under our first approximation) and represents only a tentative value.

The molecular weights of our samples are collected in Table I. The values in columns 3 and 4 are calculated using the first approximation, i.e., as for a monodisperse polymer. The values in column 5 are based on the second approximation, using values of u from column 9. The values of the second virial

Table I
Molecular Weight, Virial Coefficient, Polydispersity, and Intrinsic Viscosity of Polystyrene Samples

Sample	M^a	$M_B{}^{b,c}$ eq 26	$M_{BB}{}^d$ eq 26	$\overline{M}_{w,tot}{}^d$ eq 32	$10^4A_{2,B}{}^{b,c}$ eq 28	$10^4A_{2,BB}{}^d$ eq 28	$\overline{M}_w/\overline{M}_n{}^a$	u^d	$[\eta]_B{}^{b,c}$	$[\eta]_{BB}{}^d$
7b	37 000	35 600	35 500	35 900	7.24	6.38	<1.06	0.010	23.25	23.22
4b	110 000	117 000	114 000	116 000	5.19	5.08	<1.06	0.015	52.4	52.3
1c	200 000	186 000	181 000	184 000	4.67	4.43	<1.06	0.015	73.2	72.0
3b	390 000	372 000	366 000	392 000	3.65	3.17	<1.10	0.07	126.7	123.9
13a	670 000	596 000	596 000	702 000	3.32	2.97	<1.15	0.17	179.4	179.4
14b	2 000 000	1 750 000[e]	1 750 000[e]	2 840 000	2.22	2.15	<1.20	0.55		460.3[f]

[a] Manufacturer's value. [b] In benzene. [c] Reevaluated from previous studies. [d] In bromobenzene. [e] In ethyl acetate. [f] Uncorrected for shear dependence.

Table II
Experimental Values of Parameter *F* for Polystyrene in Bromobenzene

	F					
	7b	**4b**	**1c**	**3b**	**13a**	**14b**
M_{BB}	35 500	114 000	181 000	366 000	596 000	1 750 000
ϕ_p						
0.000	0.4215	0.4370	0.4455	0.4610	0.4635	(0.4735)
0.001	0.4192	0.4351	0.4422	0.4550	0.4580	0.4652
0.002	0.4170	0.4332	0.4390	0.4490	0.4505	0.4570
0.004	0.4135	0.4295	0.4342	0.4420	0.4425	0.4480
0.006	0.4100	0.4260	0.4305	0.4355	0.4370	0.4420
0.008	0.4080	0.4232	0.4265	0.4315	0.4325	0.4370
0.010	0.4060	0.4205	0.4230	0.4280	0.4285	0.4325
0.012	0.4040	0.4180	0.4203	0.4250	0.4255	0.4283
0.016	0.4000	0.4131	0.4153	0.4195	0.4198	0.4215
0.020	0.3966	0.4087	0.4108	0.4145	0.4149	0.4158
0.024	0.3935	0.4048	0.4070	0.4105	0.4105	0.4115
0.028	0.3905	0.4014	0.4034	0.4065	0.4065	0.4078
0.032	0.3880	0.3984	0.4000	0.4029	0.4028	0.4045
0.036	0.3857	0.3956	0.3971	0.3996	0.3996	0.4015
0.040	0.3835	0.3928	0.3944	0.3965	0.3967	0.3985
0.044	0.3813	0.3902	0.3916	0.3935	0.3942	0.3957
0.048	0.3793	0.3877	0.3891	0.3909	0.3918	0.3932
0.052	0.3773	0.3855	0.3870	0.3890	0.3895	0.3908
0.056	0.3754	0.3835	0.3850	0.3870	0.3875	0.3885
0.060	0.3738	0.3815	0.3830	0.3855	0.3855	0.3865
0.064	0.3722	0.3795	0.3810	0.3839	0.3835	0.3849
0.068	0.3706	0.3775	0.3792		0.3818	0.3832
0.072	0.3690	0.3755	0.3777		0.3805	0.3817
0.076	0.3675					0.3805

coefficient (columns 6 and 7) are based on the first approximation. The virial coefficients as well as intrinsic viscosities (last two columns) are quite close for solutions in benzene and in bromobenzene. The Mark–Houwink–Sakurada relation for polystyrene in bromobenzene was found to be

$$[\eta]_{BB} = 1.19 \times 10^{-2} M^{0.72} \quad (36)$$

as compared with the relation for polystyrene in benzene[4]

$$[\eta]_B = 1.23 \times 10^{-2} M^{0.72} \quad (37)$$

In these relations, the subscripts B and BB represent benzene and bromobenzene, respectively.

The values of F were calculated using our second approximation for at least three equilibrium photographs and several hundred experimental points per photograph. The data were plotted in a single plot F vs. ϕ_p and a single line drawn through the points; most points deviated from the line by less than 0.002. The superposition of data from the short and long column runs was very good for the intermediate concentrations; for the lowest concentrations the values from the short column runs were relied upon. The values of F, which were interpolated on the smooth lines, are collected in Table II and plotted in Figure 5.

The interaction parameter χ may be obtained by integration of eq 13 as

$$\chi = \frac{2}{\phi_p^2} \int_0^{\phi_p} F \phi_p \, d\phi_p \quad (38)$$

The values of χ are reported in Table III and plotted in Figure 6.

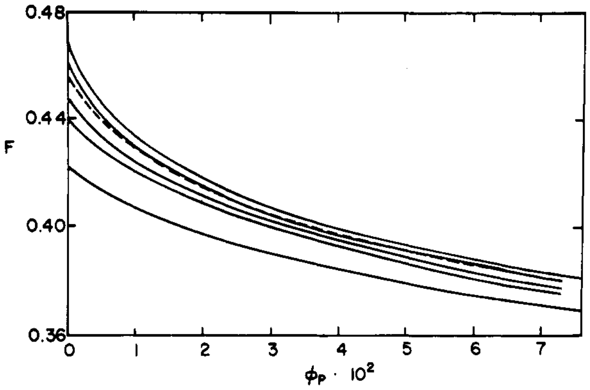

Figure 5. Plot of parameter F vs. ϕ_p. Polystyrene samples (from bottom to top) **7b, 4b, 1c, 3b** (broken line), **13a,** and **14b** in bromobenzene.

Discussion

The most elaborate theory of the dependence of the function g on the molecular weight and concentration of the polymer is the theory of Koningsveld et al.[2] According to this theory, the function g (and similarly functions χ and F) may be split into two parts: (i) a term g_c, which is characteristic for concentrated solutions and is common for all molecular weights, and (ii) a term g_e, which characterizes the excluded volume effect at low concentrations (and, consequently, depends on molecular weight) and which vanishes exponentially at higher concentrations. The relevant relations are

$$g = g_c + g_e \quad (39)$$

$$g_c = \alpha + \beta/(1 - \Gamma\phi_p) \quad (40)$$

$$g_e = g^*(\overline{M}) \exp(-\lambda(\overline{M})\phi_p) \quad (41)$$

The parameters β and Γ are positive constants for most polymers; $\lambda(\overline{M})$ is a positive function, which increases with increasing molecular weight; $g^*(\overline{M})$ for good solvents is a positive function such that the product $g^*(1 + \lambda)$ increases with increasing molecular weight. In our previous study,[1] we have shown that these properties imply that (i) g_c, χ_c, and F_c are increasing functions of concentration and, consequently, also g, χ, and F are increasing functions of concentration in

Table III
Experimental Values of Function χ for Polystyrene in Bromobenzene

	χ					
	7b	**4b**	**1c**	**3b**	**13a**	**14b**
M_{BB}	35 500	114 000	181 000	366 000	596 000	1 750 000
ϕ_p						
0.000	0.4215	0.4370	0.4455	0.4610	0.4635	(0.4735)
0.001	0.4200	0.4357	0.4428	0.4570	0.4591	0.4680
0.002	0.4185	0.4345	0.4412	0.4530	0.4548	0.4625
0.004	0.4159	0.4320	0.4375	0.4471	0.4482	0.4546
0.006	0.4135	0.4296	0.4346	0.4423	0.4434	0.4492
0.008	0.4115	0.4274	0.4319	0.4384	0.4396	0.4449
0.010	0.4099	0.4254	0.4293	0.4353	0.4363	0.4412
0.012	0.4084	0.4235	0.4269	0.4326	0.4334	0.4379
0.016	0.4055	0.4199	0.4229	0.4280	0.4286	0.4321
0.020	0.4029	0.4166	0.4193	0.4240	0.4245	0.4272
0.024	0.4005	0.4136	0.4161	0.4205	0.4209	0.4230
0.028	0.3982	0.4108	0.4132	0.4173	0.4176	0.4195
0.032	0.3961	0.4082	0.4105	0.4143	0.4145	0.4163
0.036	0.3942	0.4059	0.4080	0.4116	0.4117	0.4135
0.040	0.3923	0.4036	0.4056	0.4090	0.4091	0.4109
0.044	0.3906	0.4015	0.4034	0.4066	0.4068	0.4085
0.048	0.3890	0.3995	0.4013	0.4042	0.4046	0.4063
0.052	0.3874	0.3976	0.3994	0.4021	0.4025	0.4038
0.056	0.3859	0.3958	0.3975	0.4002	0.4006	0.4015
0.060	0.3844	0.3941	0.3958	0.3984	0.3987	0.3997
0.064	0.3830	0.3924	0.3941	0.3967	0.3970	0.3980
0.068	0.3817	0.3908	0.3925		0.3954	0.3964
0.072	0.3804	0.3893	0.3910		0.3938	0.3949
0.076	0.3792					0.3939

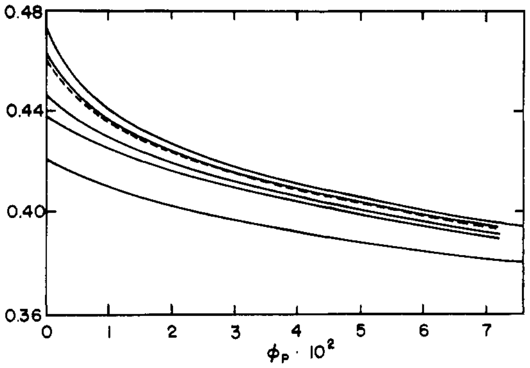

Figure 6. Plot of parameter χ vs. ϕ_p for polystyrene in bromobenzene. Lines in the same order as in Figure 5.

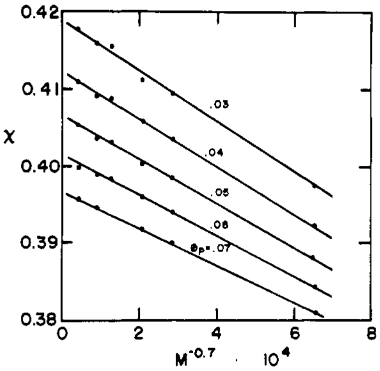

Figure 7. Dependence of parameter χ on $M^{-0.7}$ for several values of ϕ_p. Polystyrene in bromobenzene.

the region of high concentrations; (ii) the dependences of χ and F on concentration for different molecular weights merge together in the region of high concentrations; and (iii) the dependences of F on concentration cross each other before finally merging together.

Our experimental data do not corroborate these predictions. The lines in Figures 5 and 6 do not approach each other; in fact, they seem to be parallel in the region of higher concentrations. This behavior is still more visible in Figure 7, where χ is plotted vs. $M^{-0.7}$ for several values of ϕ_p. ($M^{-0.7}$ was chosen as abscissa, because it resulted in the best linearity of the plot). The lines in Figure 7 for higher concentration are almost parallel indicating that the F values are not going to approach each other any more. We must therefore conclude that the term g_c describing the concentrated solutions is still dependent on molecular weight. Moreover, the functions F_c and χ_c are obviously decreasing with increasing concentration in another departure from the above theory. The older data of Scholte[10] for polystyrene in toluene, while much less detailed than the present data, are in good agreement with the present observation.

In the region of lower concentrations, the dependences of F and χ on concentration diverge for different samples in a qualitative agreement with the theory of the excluded volume term g_e.

We have reexamined the experimental data for polystyrene in benzene, reported in our previous study.[1] They remain essentially unchanged when the polydispersity is taken into account using our second approximation. However, when the data are viewed from the standpoint of the present observations, they are strikingly similar: (i) the F values for different molecular weights approach each other with increasing concentration very slowly and (ii) the F and χ values are decreasing with increasing concentration for all molecular weights at all concentrations. In the benzene study we were able to force a partial agreement of experimental data with relations 39–41 due to a limited range of employed concentrations. Such a forced fit, however, proved impossible for present data in an extended region of concentrations.

Conclusions

The experimental values of χ and F are functions of molecular weight even at concentrations around 7 vol %. There does not seem to be a tendency that they will become independent of molecular weight even at still higher concentration. Both F and χ are monotonically decreasing functions of concentration up to at least 7 vol %. These observations are not a result of a possible improper treatment of polydispersity; polydispersity has hardly any effect on the evaluation of F in this region of concentrations. While the spread of both F and χ values for all our samples at higher concentrations is not very large (about 0.015), it seems to be, nevertheless, experimentally well established.

These experimental facts suggest that the accepted theory of function g, as formulated by Koningsveld et al.,[2] may need some modification. Specifically, the term g_c should be reformulated to allow for its dependence on molecular weight and for its decrease with increasing concentration. The excess term g_e may require modification too; the rate of decrease of F with concentration in the *low* concentration region does not seem to depend on molecular weight as much as required by the theory.

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Thermodynamic Analysis of an Ethylene and Vinyl Acetate Copolymer with Various Solvents by Gas Chromatography

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ABSTRACT: We have obtained infinite-dilution properties of an ethylene–vinyl acetate copolymer containing 29 wt % vinyl acetate with 43 volatile solvents at 150.46 and 160.53 °C. We have calculated heats of solution, infinite-dilution activity coefficients, Flory–Huggins interaction parameters, and molar Gibbs energies of absorption for the 43 solvents at essentially infinite dilution of solvent from raw data obtained by gas–liquid chromatography. The heats of solution are resolved into their dispersion component, permanent dipole interaction component, and specific interaction component using a simple, general method. We show that information obtained from decomposition of the heats of solution can be used, in much the same way as Hansen's three-dimensional solubility parameter method, to explain otherwise anomalous interactions of solvents with a polar polymer. Additionally, an important conclusion is drawn regarding sample sizes and flow rates required to obtain reliable thermodynamic information from gas–liquid chromatography using polar solvents.

Although some data are available in the literature, thermodynamic interactions between polar polymers and solvents have not been studied in great detail for cases in which the polymer/solvent mixture is almost pure polymer. The purpose of this work is to show how the interactions between small amounts of solvents and a polar polymer can be determined experimentally and how the data can be resolved into the contributions of dispersion forces, polar forces, and specific interactions using a general method of analysis not linked to any specific theoretical method. The analysis we use provides an alternative to the semiquantitative Hansen three-dimensional solubility parameter approach for solutions of polar polymers.

The polymer we have chosen to use is a slightly polar polymer: ethylene–vinyl acetate copolymer (EVA). EVA is a simple, random copolymer with a glass-transition temperature well below room temperature. The vinyl acetate moiety in the polymer backbone provides the possibility of relatively strong specific interactions with certain solvents and polar interactions with other solvents. Also, the melting point of EVA is sufficiently low that it is not difficult to work with the molten polymer.

In order to determine the thermodynamic quantities needed for our analysis, we used gas–liquid chromatography (GLC). GLC has long been recognized[1,2] as an attractive alternative and rapid method to obtain thermodynamic properties.[3]

Experimental Section

Equipment. A Carle AG 311 GC with a thermal conductivity detector was used in this study. A Fisher Recordall Series 5000 recorder was used to record the response from the detector. An Instrulab Digital Thermometer with a precision of ±0.01 °C was used to read the oven temperature. The inlet pressure to the column was measured by a Seegers 0–30 psi pressure gauge which had a precision of ±0.1 psi. Helium was used as the carrier gas, and it passed through a gas purifier containing molecular sieves before it entered the chromatograph. The flow rate of the carrier gas was measured using a 1.2-cm i.d. soap-film flow meter. The flow rate of gas through the GC was controlled by flow controllers installed in the chromatograph.

Column Preparation. The column, a ⅛-in. o.d. stainless steel tube, was filled with 0.2876 g of EVA copolymer coated on 80–100 mesh Fluoropak-80 (a powdered Teflon) with a loading (weight of polymer per weight of polymer and support × 100) of 14.75%. Fluoropak-80 is a suitable support for polar-solute measurements since it gives nearly symmetric retention curves indicating minimal substrate adsorptive capacity.[4,5]

The EVA copolymer, 29% by weight vinyl acetate, was supplied by Dr. Samil Beret of Union Carbide Corp. The sample designation was DX-31034. DX-31034 is a random copolymer of ethylene and vinyl acetate produced by free-radical polymerization in a tubular reactor at high pressure. The number average molecular weight is 43200 g/g

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