Macromolecules **1980,** *13,* 1215-1220

the local derivative of the concentration at the boundary point is

$$\frac{d\Theta^*}{d\xi^*} = \left[\frac{\partial\Theta}{\partial\xi} + \frac{\partial\Theta}{\partial\tau}\frac{d\tau}{d\xi}\right]^* \qquad (3')$$

In the right-hand member the asterisk indicates that the derivatives must be specified for the boundary point.

In view of the initial conditions $\Theta = 1$ ($\tau = 0$, $\xi > 0$) and $\xi^* = 0$ ($\tau = 0$), we have

$$\partial\Theta/\partial\xi = 0 \qquad (\xi^* = 0) \qquad (4')$$

The balance equation for the solute, going with eq 6, is

$$\frac{\partial\Theta}{\partial\tau} = -\frac{\partial}{\partial\xi}\left\{\frac{(1+\xi)\Theta}{(1+m\xi)(1+\gamma\Theta)}\right\} \qquad (5')$$

Expanding the right-hand member and using (4′), we observe that

$$(\partial\Theta/\partial\tau)^* = -(1-m)/(1+\gamma) \qquad (\xi^* = 0) \qquad (6')$$

It follows from (6) that

$$d\xi^*/dT = (1+\gamma)^{-1} \qquad (\xi^* = 0) \qquad (7')$$

Substituting (4′), (6′), and (7′) into (3′) we obtain

$$d\Theta^*/d\xi^* = -(1-m) \qquad (\xi^* = 0) \qquad (8')$$

This initial value holds good irrespective of the presence of a concentration effect. It is fulfilled by (2′). If (2′) were to be augmented by a term of the order $\gamma_i m \xi_i$, then condition 8′ could not be satisfied. On this ground we conclude that $n \geq 2$.

References and Notes

(1) H. J. Cantow, *Makromol. Chem.*, **30**, 169 (1959).
(2) M. Wales and S. J. Rehfeld, *J. Polym. Sci.*, **62**, 179 (1962).
(3) I. H. Billick, *J. Phys. Chem.*, **66**, 1941 (1962).
(4) I. H. Billick, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **5**, 855 (1964).
(5) T. Homma et al., *Makromol. Chem.*, **67**, 132 (1963).
(6) J. E. Blair, *J. Polym. Sci., Part C*, **8**, 287 (1965).
(7) W. J. Closs, B. R. Jennings, and H. G. Jerrard, *Eur. Polym. J.*, **4**, 639 (1968).
(8) V. Petrus, I. Danihel, and M. Bohdanecky, *Eur. Polym. J.*, **7**, 143 (1971).
(9) A. Kotera, T. Saito, and T. Hamada, *Polym. J.*, **3**, 421 (1972).
(10) A. Haug and G. Meyerhoff, *Makromol. Chem.*, **53**, 91 (1962).
(11) J. Llopis, A. Albert, and P. Usobiago, *Eur. Polym. J.*, **3**, 259 (1967).
(12) M. Abe et al., *Bull. Chem. Soc. Jpn.*, **41**, 2330 (1968).
(13) H. Yamakawa, *J. Chem. Phys.*, **36**, 2995 (1962).
(14) C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **41**, 937 (1964).
(15) K. F. Freed, *J. Chem. Phys.*, **52**, 4212 (1976).
(16) H. Svensson, *Opt. Acta*, **1**, 25 (1954).
(17) J. M. Cowie and S. Bywater, *Polymer*, **6**, 197 (1965).
(18) G. V. Schulz and M. Hoffman, *Makromol. Chem.*, **23**, 220 (1957).
(19) J. J. H. Mulderije, to be published in *Macromolecules*.
(20) "Handbook of Chemistry and Physics", 52nd ed., CRC Press, Cleveland, Ohio, 1971.
(21) S. Imai, *J. Chem. Phys.*, **52**, 4212 (1970).
(22) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).
(23) I. Noda et al., *J. Phys. Chem.*, **71**, 4048 (1967).
(24) I. Noda, K. Mizutani, and T. Kato, *Macromolecules*, **10**, 618 (1977).
(25) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969, Chapter 2.
(26) T. A. Orofino and A. Ciferri, *J. Phys. Chem.*, **68**, 3136 (1964).
(27) See H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971.
(28) A. R. Shultz and P. J. Flory, *J. Polym. Sci.*, **15**, 231 (1955).
(29) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).
(30) A. Yamamoto et al., *Polym. J.*, **2**, 799 (1971).
(31) M. Kurata and H. Yamakawa, *J. Chem. Phys.*, **29**, 311 (1958); H. Yamakawa and M. Kurata, *J. Phys. Soc. Jpn.*, **13**, 94 (1958).
(32) T. Kato et al., *Macromolecules*, **3**, 777 (1970).
(33) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).
(34) G. C. Berry, *J. Polym. Sci., Part B*, **4**, 161 (1966).
(35) H. Fujita et al., *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 2255 (1977).
(36) J. Shimada and H. Yamakawa, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1927 (1978).
(37) W. H. Stockmayer and A. C. Albrecht, *J. Polym. Sci.*, **32**, 215 (1958).
(38) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **55**, 3188 (1971).
(39) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(40) J. E. Hearst, *J. Chem. Phys.*, **37**, 2547 (1962).
(41) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
(42) H. A. Scheraga and L. Mandelkern, *J. Am. Chem. Soc.*, **75**, 179 (1953).
(43) See ref 27, p 298.
(44) G. C. Berry, *J. Chem. Phys.*, **46**, 1338 (1967).
(45) J. M. G. Cowie, S. Bywater, and D. J. Worsfold, *Polymer*, **8**, 105 (1967).
(46) J. M. G. Cowie and S. Bywater, *J. Polym. Sci., Part C*, **30**, 85 (1970).
(47) B. Nyström and J. Roots, *Eur. Polym. J.*, **14**, 551 (1978).
(48) I. Noda et al., *Macromolecules*, **3**, 787 (1970).
(49) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).
(50) A. F. V. Eriksson, *Acta Chem. Scand.*, **10**, 360 (1956).

Sedimentation Equilibrium of Highly Nonideal Solutions of Polydisperse Polymers

Petr Munk

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

Received September 10, 1979

ABSTRACT: A new method of analysis is proposed for determination of the average molecular weight of a polymer sample, of its polydispersity, and of the thermodynamic characteristics of its solution. The method involves only a single sedimentation equilibrium experiment in the ultracentrifuge and is applicable even to highly nonideal solutions. It is based on the assumptions that (1) the distribution function of the polymer sample is reasonably well described by the unimodal function of the Schulz-Zimm type and that (2) the thermodynamic behavior of the solution obeys the same formula which was found useful for monodisperse samples. The method yielded plausible results both for highly nonideal solutions of polystyrene samples with a narrow distribution of molecular weights and for unfractionated samples of polyacrylamide with a broader distribution.

Among the methods used for studying polymer solutions, the method of sedimentation equilibrium is potentially the most precise. Using interference optics, sapphire cell windows, and an automated plate reader, we can, under favorable circumstances, measure the profile (one hundred and more experimental points) of concentration and concentration gradient within the cell with a precision of 1-2%. Why is then this method so rarely used for the

0024-9297/80/2213-1215$01.00/0

characterization of polymer materials?

The reason is in the somewhat difficult analysis of the experimental data. Both the polydispersity of the polymer sample and the nonideality of the solution strongly influence the concentration profile. Even for ideal solutions, i.e., for a case where the thermodynamic behavior of the solution is supposed to be precisely known, the molecular weight and its distribution may be obtained (with an impressive precision) only when several equilibrium runs are made.[1,2] The analysis becomes even more complicated when moderately nonideal solutions are involved.[3] Such measurements become extremely time consuming.

It is attractive to consider the feasibility of an analysis of a single equilibrium run. We have shown that for a monodisperse polymer the molecular weight and the thermodynamic behavior over an extended concentration region can be obtained with a good precision from a single equilibrium run.[4,5] We have also shown that such an analysis may be performed even on polydisperse samples, provided that the molecular weight distribution is rather narrow. In fact, we were able to estimate the polydispersity parameter together with the thermodynamic data.[6]

Would it then be possible to obtain routinely the molecular weight, polydispersity, and thermodynamic data from a single equilibrium run? Obviously, some assumptions must be made about both the polydispersity and thermodynamic behavior. In this paper we show that we may formulate such assumptions sufficiently broadly to cover a rather large and important class of polymer samples, namely, those with a unimodal distribution of molecular weights.

Theoretical Analysis

In a previous paper[6] we have shown that the variation of the local average molecular weight with the local concentration of polymer within the cell of the ultracentrifuge at equilibrium is a unique function of the local polydispersity of the polymer. This relation was derived by assuming that the free enthalpy of mixing ΔG_{mix} for the polymer solution might be written as

$$\Delta G_{\mathrm{mix}}/RT = n_s \ln \phi_s + \sum_i n_i \ln \phi_i + n_s \phi_p g \qquad (1)$$

In the first part of the present analysis we show some important consequences of this unique dependence. Then we show that the relation is still approximately valid when a more general relation is used for ΔG_{mix}. In the latter part, we suggest a convenient phenomenological expression for the description of the thermodynamic behavior of highly nonideal solutions. Finally, we combine all these elements into a method for simultaneous evaluation of molecular weight, polydispersity, and thermodynamic parameters from a single sedimentation equilibrium experiment with a highly nonideal solution of a polydisperse polymer.

In eq 1 n denotes the number of moles and ϕ the volume fraction. The subscript s refers to the solvent, the subscript i to an individual polymer component, and the subscript p to a concentration variable summed over all polymer components. RT has its usual meaning and P is pressure. For simplicity, we neglect any changes of volume of mixing. In the following, the symbol c represents the concentration in g/mL, ρ is density, V_i is the molar volume of the ith component, and M_i is its molecular weight. The specific volume v is the same for all polymer components. The above quantities are related by relations 2–5.

$$\phi_j = n_j V_j / (n_s V_s + \sum_i n_i V_i) \qquad (2)$$

$$V_i = M_i v \qquad (3)$$

$$\phi_i = c_i v \qquad (4)$$

$$(1 - v\rho) = (1 - v\rho_s)\phi_s \qquad (5)$$

The function g in eq 1 characterizes the thermodynamic behavior of the polymer solution. In our previous paper,[6] we performed the calculations by assuming that, for a given polymer sample, g is a function only of ϕ_p and is not influenced by the redistribution of molecular weights along the column in sedimentation equilibrium experiments.

In that case, the chemical potential differences $\Delta\mu_j$ are easily obtained by differentiating ΔG_{mix} as

$$\Delta\mu_s/RT = \ln \phi_s + \phi_p - V_s \sum_k (\phi_k/V_k) + \phi_p^2 \chi \qquad (6)$$

$$\Delta\mu_i/RT = \ln \phi_i + 1 - V_i\phi_s/V_s + V_i \sum_k (\phi_k/V_k) + V_i \phi_s^2 X/V_s \qquad (7)$$

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

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

Further differentiation yields

$$(\partial \mu_i/\partial c_k)_{P,T} = RT[\delta_{ik}/c_i + V_i v/V_s - V_i v/V_k - 2F\phi_s V_i v/V_s] \qquad (10)$$

$$F \equiv \chi + (\phi_p/2)(\partial \chi/\partial \phi_p)_{P,T} \equiv X - (\phi_s/2)(\partial X/\partial \phi_p)_{P,T} \qquad (11)$$

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

The condition for equilibrium in an ultracentrifuge for each polymer component reads

$$M_i (1 - v\rho)\omega^2 r = \sum_k (\partial \mu_i/\partial c_k)_{P,T} (\mathrm{d}c_k/\mathrm{d}r) \qquad (12)$$

where ω is the angular velocity of the rotor and r is the distance from the rotor axis. Substitution of eq 10 into eq 12 yields

$$M_i(1 - v\rho)\omega^2 r/RT = (1/c_i)(\mathrm{d}c_i/\mathrm{d}r) + (V_i v/V_s)\sum_k [1 - V_s/V_k - 2F\phi_s](\mathrm{d}c_k/\mathrm{d}r) \qquad (13)$$

Substitution of eq 3 into eq 13 and slight rearrangement leads to

$$c_i M_i B(r) = \mathrm{d}c_i/\mathrm{d}r \qquad (14)$$

$$B(r) \equiv (1 - v\rho)\omega^2 r/RT - (v^2/V_s)\sum_k [1 - V_s/V_k - 2F\phi_s](\mathrm{d}c_k/\mathrm{d}r) \qquad (15)$$

Obviously, the function $B(r)$, while dependent on the local composition of the solution, is common for all components of the solute. Summation of both sides of eq 14 over all polymer species yields

$$c_p \bar{M}_w B(r) = \mathrm{d}c_p/\mathrm{d}r \qquad (16)$$

Multiplication of eq 14 by M_i and summation yields

$$c_p \bar{M}_w \bar{M}_z B(r) = \sum_i \mathrm{d}(c_i M_i)/\mathrm{d}r = \mathrm{d}(c_p \bar{M}_w)/\mathrm{d}r = \bar{M}_w(\mathrm{d}c_p/\mathrm{d}r) + c_p(\mathrm{d}\bar{M}_w/\mathrm{d}c_p)(\mathrm{d}c_p/\mathrm{d}r) \qquad (17)$$

During the derivation of eq 16 and 17 the usual definitions of the weight-average molecular weight $\bar{M}_w$ and of the Z-average molecular weight $\bar{M}_z$ were employed. Elimination of $B(r)$ from eq 16 and 17 yields relation 18, which is

$$\mathrm{d} \ln \bar{M}_w/\mathrm{d} \ln c_p = (\bar{M}_z/\bar{M}_w) - 1 \equiv u \qquad (18)$$

independent of the thermodynamic properties of the solution. In our previous paper[6] we assumed that the parameter u defined by eq 18 does not vary along the solution column. We now show that for one important type of the distribution function of molecular weights, namely, the

Schulz–Zimm distribution, the constancy of u follows from the above analysis.

Integrating eq 14 from the meniscus (superscript m) we get

$$c_i = c_i^{\mathrm{m}} \exp\left[M_i \int_{r^{\mathrm{m}}}^{r} B(r)\,\mathrm{d}r\right] \tag{19}$$

Switching now from a discrete distribution of molecular weights to a continuous one ($c_i \rightarrow \mathrm{d}c_{\mathrm{p}}$; $M_i \rightarrow M$), we write for the distribution of molecular weights at the meniscus the Schulz–Zimm expression

$$c_i^{\mathrm{m}} \equiv \mathrm{d}c_{\mathrm{p}}^{\mathrm{m}} = c_{\mathrm{p}}^{\mathrm{m}}[b^{z+1}/\Gamma(z+1)]M^z \exp(-bM)\,\mathrm{d}M \tag{20}$$

$$b = (z+1)/\bar{M}_{\mathrm{w}} \tag{21}$$

In eq 20 $\Gamma(x)$ is the gamma function; the parameters z and b as well as $\bar{M}_{\mathrm{w}}$ refer to the distribution at the meniscus. The parameter z is a characteristic of the width of the distribution; it is related to the parameter u as

$$u = 1/(z+1) \tag{22}$$

Substituting eq 20 into eq 19, we get

$$c_i \equiv \mathrm{d}c_{\mathrm{p}} = c_{\mathrm{p}}^{\mathrm{m}}[b^{z+1}/\Gamma(z+1)]M^z \exp\left\{-M\left[b - \int_{r^{\mathrm{m}}}^{r} B(r)\,\mathrm{d}r\right]\right\}\mathrm{d}M \tag{23}$$

Obviously, the functional form of eq 23 is the same as the form of eq 20. Specifically, the characteristic parameter z (and consequently u) remains the same for any position in the cell, proving our claim.

What is now the relation of the distribution function at arbitrary point in the cell to the original distribution function of the whole polymer sample? While we were not able to find a general answer, the answer proved to be simple for one special case. Let us assume that the sedimentation equilibrium has been established at a rotor velocity high enough so that concentration of all polymer species at the meniscus is negligible. Let us also assume that the polymer solution is pseudoideal; the concentration profile of a component is not influenced by the presence of other components and the higher virial terms are absent. Then the concentration of the ith component in the cell may be written as

$$c_i = c_i^{\mathrm{b}} \exp[M_i(1 - v\rho_{\mathrm{s}})\omega^2(r^2 - (r^{\mathrm{b}})^2)/2RT] \tag{24}$$

where the superscript b refers to the bottom of the cell. Integrating over the volume of the sector-shaped cell, we get for the total mass of the ith component in the cell, m_i

$$\begin{aligned} m_i &= \int_{r^{\mathrm{m}}}^{r^{\mathrm{b}}} kc_ir\,\mathrm{d}r \\ &= \frac{kRTc_i^{\mathrm{b}}}{M_i(1 - v\rho_{\mathrm{s}})\omega^2} \left\{1 - \exp\left[\frac{M_i(1 - v\rho_{\mathrm{s}})\omega^2}{2RT}((r^{\mathrm{m}})^2 - (r^{\mathrm{b}})^2)\right]\right\} \end{aligned} \tag{25}$$

where k is an inconsequential geometric factor. Under the conditions of high-speed equilibrium, the exponential term in eq 25 is negligible when compared to unity. Switching now to a continuous distribution of molecular weights and substituting for $c_i^{\mathrm{b}} \equiv \mathrm{d}c^{\mathrm{b}}$ the Schulz–Zimm expression as in eq 20, we get

$$m_i \equiv \mathrm{d}m = c_{\mathrm{p}}^{\mathrm{b}}[b^{z+1}/\Gamma(z+1)][kRT/\omega^2(1 - v\rho_{\mathrm{s}})]M^{z-1} \exp(-bM)\,\mathrm{d}M \tag{26}$$

Equation 26 represents the distribution of the original sample. It is again of the Schulz–Zimm type. The characteristic parameter $z' \equiv z - 1$ of this distribution is smaller than the corresponding parameter at an arbitrary point in the cell: the distribution function of the original sample is broader than that of the redistributed one.

For the more general case of nonideal solutions and nonnegligible meniscus concentrations we expect the difference between the characteristic parameters for the local and overall distribution to become even less while the unimodal character will remain qualitatively the same.

In the above derivations we assumed that the interaction function g does not change with the change of the molecular weight and/or its distribution. That assumption implies that all the virial coefficients are independent of molecular weight. While this may be a fair assumption for the second virial coefficient, the third virial coefficient is known to increase more or less proportionately to the molecular weight. In the following paragraphs, we propose a more realistic expression for the interaction terms and we study what effect this change has on eq 18.

Let us assume that the expression for ΔG_{mix} has the form

$$\Delta G_{\mathrm{mix}}/RT = n_{\mathrm{s}} \ln \phi_{\mathrm{s}} + \sum_i n_i \ln \phi_i + n_{\mathrm{s}}\sum_i \phi_i g_i \tag{27}$$

Here, each polymer species has a corresponding interaction function g_i. However, to keep the computation manageable, we assume that every g_i is a function only of the total concentration ϕ_{p}. The functions for different i's are, of course, different. Routine calculations now lead to the expression

$$\begin{aligned} (\partial\mu_i/\partial c_k)_{P,T} = RT\{&\delta_{ik}/c_i + (V_iv/V_{\mathrm{s}}) \times \\ &[1 - V_{\mathrm{s}}/V_k - g_i - \phi_{\mathrm{s}}g_k + \sum_j g_j\phi_j + \phi_{\mathrm{s}}(\mathrm{d}g_i/\mathrm{d}\phi_{\mathrm{p}}) + \\ &\phi_{\mathrm{s}}^2(\mathrm{d}g_k/\mathrm{d}\phi_{\mathrm{p}}) - 3\phi_{\mathrm{s}}\sum_j \phi_j(\mathrm{d}g_j/\mathrm{d}\phi_{\mathrm{p}}) + \phi_{\mathrm{s}}^2\sum_j \phi_j(\mathrm{d}^2g_j/\mathrm{d}\phi_{\mathrm{p}}^2)]\} \end{aligned} \tag{28}$$

Substitution of eq 28 into eq 12 yields, after some simplifications

$$c_iM_iB'(r) = \mathrm{d}c_i/\mathrm{d}r - M_i\chi_ic_i(v^2/V_{\mathrm{s}})\,\mathrm{d}c_{\mathrm{p}}/\mathrm{d}r \tag{29}$$

$$\begin{aligned} B'(r) \equiv (1 - v\rho)\omega^2r/RT - (v^2/V_{\mathrm{s}})\{&(\mathrm{d}c_{\mathrm{p}}/\mathrm{d}r) \times \\ &[1 - \sum_k g_k\phi_k - 3\phi_{\mathrm{s}}\sum_k \mathrm{d}g_k/\mathrm{d}\phi_{\mathrm{p}} + \phi_{\mathrm{s}}^2\sum_k \mathrm{d}^2g_k/\mathrm{d}\phi_{\mathrm{p}}^2] - \\ &\sum_k (\mathrm{d}c_k/\mathrm{d}r)[V_{\mathrm{s}}/V_k + \phi_{\mathrm{s}}g_k - \phi_{\mathrm{s}}^2\,\mathrm{d}g_k/\mathrm{d}\phi_{\mathrm{p}}]\} \end{aligned} \tag{30}$$

$$\chi_i \equiv g_i - \phi_{\mathrm{s}}(\mathrm{d}g_i/\mathrm{d}\phi_{\mathrm{p}}) \tag{31}$$

Summation of eq 29 over all polymer species yields

$$c_{\mathrm{p}}\bar{M}_{\mathrm{w}}B'(r) = (\mathrm{d}c_{\mathrm{p}}/\mathrm{d}r)[1 - (v^2/V_{\mathrm{s}})\sum_i M_i\chi_ic_i] \tag{32}$$

while multiplication by M_i and summation yields

$$c_{\mathrm{p}}\bar{M}_{\mathrm{z}}\bar{M}_{\mathrm{w}}B'(r) = (\mathrm{d}c_{\mathrm{p}}/\mathrm{d}r)[\bar{M}_{\mathrm{w}} + c_{\mathrm{p}}\,\mathrm{d}\bar{M}_{\mathrm{w}}/\mathrm{d}c_{\mathrm{p}} - (\mathrm{v}^2/V_{\mathrm{s}})\sum_i M_i^2\chi_ic_i] \tag{33}$$

Elimination of $B'(r)$ from eq 32 and 33 leads to

$$\mathrm{d} \ln \bar{M}_{\mathrm{w}}/\mathrm{d} \ln c_{\mathrm{p}} = (\bar{M}_{\mathrm{z}}/\bar{M}_{\mathrm{w}}) - 1 - (v^2/\bar{M}_{\mathrm{w}}V_{\mathrm{s}})\sum_i (\bar{M}_{\mathrm{z}} - M_i)M_i\chi_ic_i \tag{34}$$

If χ_i is independent of molecular weight, the last term in eq 34 vanishes, reducing eq 34 to eq 18. For the estimate of the significance of the last term of eq 34 we need to estimate the dependence of χ_i on molecular weight. In our previous paper[6] we found that for polystyrene in bromobenzene (a good solvent) χ is decreasing linearly with $M^{-0.7}$. More generally, let us assume

$$\chi = \alpha_\chi - \beta_\chi M^{-\gamma_\chi} \qquad (35)$$

For polystyrene in bromobenzene, $\gamma_\chi = 0.7$ and β_χ is a slowly decreasing function of concentration approximately equal to 30. We expect that for poorer solvents β_χ would be less. Assuming again the Schulz–Zimm distribution, we get after a straightforward but tedious calculation eq 36.

$$\mathrm{d}\ln \bar{M}_\mathrm{w}/\mathrm{d}\ln c_\mathrm{p} = (z+1)^{-1}[1 + (v^2/V_\mathrm{s})\beta_\chi c_\mathrm{p}\bar{M}_\mathrm{w}^{1-\gamma_\chi}\{\gamma_\chi(z+1)^{\gamma_\chi}\Gamma(z+2-\gamma_\chi)/\Gamma(z+2)\}] \qquad (36)$$

The expression in braces in eq 36 is smaller than unity; $(z+1)^{-1} \equiv u$. Thus, the effect of variation of χ with molecular weight may be neglected if the product $(v^2/V_\mathrm{s})\beta_\chi c_\mathrm{p}\bar{M}_\mathrm{w}^{1-\gamma_\chi}$ is sufficiently smaller than unity. The approximation gets worse with increasing molecular weight and concentration. For polystyrene in bromobenzene, the approximation still seems to be acceptable for $M = 10^6$ and $c_\mathrm{p} < 0.01$ g/mL. For polymer–solvent systems which are not so good thermodynamically, we expect the limits of applicability to be still broader.

At this point we summarize the foregoing analysis as follows: for those polymer samples which are reasonably well described by the Schulz–Zimm distribution function of molecular weights and are studied at appropriately low concentrations, relation 18 with a constant value of u is a fair description of the molecular-weight profile in the sedimentation cell at equilibrium. Thus, under such circumstances, we may integrate eq 18 to obtain

$$\bar{M}_\mathrm{w} = Kc_\mathrm{p}^{u} \qquad (37)$$

Knowing from the experiment the distribution of concentration in the cell, we need only to find the two parameters K and u to be able to calculate both the molecular weight and the polydispersity of the *original* sample.

We now try to analyze the effect of the nonideality on the sedimentation equilibrium. Equation 16 or eq 32, which describe the equilibrium at any location in the cell, may be manipulated to yield

$$M_\mathrm{app}^{-1} \equiv (1 - v\rho_\mathrm{s})\omega^2 rc_\mathrm{p}/(RT\,\mathrm{d}c_\mathrm{p}/\mathrm{d}r) = M_\mathrm{w}^{-1}f(c_\mathrm{p}) \qquad (38)$$

Here, M_app is defined by the first part of eq 38; the function $f(c_\mathrm{p})$ expresses the thermodynamic properties of the system. The function $f(c_\mathrm{p})$ is related to the virial expansion of the osmotic pressure of the polymer solution. For monodisperse samples of polymers (subscript md), the expression $f(c_\mathrm{p})$ reads

$$f_\mathrm{md}(c_\mathrm{p}) = 1 + 2A_2M_\mathrm{md}c_\mathrm{p} + 3A_3M_\mathrm{md}^2c_\mathrm{p}^2 + \ldots \qquad (39)$$

In our previous paper[4] we analyzed two special cases. (i) When the nonideality of the sample is small, the quadratic and higher terms in eq 39 may be neglected; the plot of M_app^{-1} vs. c_p is a straight line. (ii) For larger nonidealities, the quadratic term is important. The third virial coefficient may be described as

$$A_3 = \gamma A_2^2M_\mathrm{md} \qquad (40)$$

The parameter γ frequently has a value close to $^1/_3$. In such a case, the first three terms of eq 39 form a full square: the plot of $M_\mathrm{app}^{-1/2}$ vs. c_p is a straight line. This square-root plot proved to be quite useful for our measurements on polymers with a narrow distribution of molecular weights. We have used it for the evaluation of molecular weights and second virial coefficients.[4-7] However, when we extended the measurement to still higher concentrations (i.e., stronger nonidealities), the square-root plot started curving downward.[6] In the same region of concentrations the plot M_app^{-1} vs. c_p, which was strongly curved at low concentrations, was becoming linear again. This behavior suggests that the function $f_\mathrm{md}(c_\mathrm{p})$ may be approximated well in a broad region of concentrations by an empirical relation

$$f_\mathrm{md}(c_\mathrm{p}) = (1 + \alpha M_\mathrm{md}c_\mathrm{p})^2/(1 + \beta M_\mathrm{md}c_\mathrm{p}) \qquad (41)$$

The empirical parameters α and β are related to the second virial coefficient as

$$A_2 = \alpha - (\beta/2) \qquad (42)$$

We now return to our analysis of a polydisperse polymer. We postulate that the function $f(c_\mathrm{p})$ for a polydisperse polymer may be written in analogy to eq 41 as

$$f(c_\mathrm{p}) = (1 + \alpha\bar{M}_\mathrm{w}c_\mathrm{p})^2/(1 + \beta\bar{M}_\mathrm{w}c_\mathrm{p}) \qquad (43)$$

To keep the number of adjustable parameters as low as possible, we assume that for a particular sample the same values of α and β are applicable at all locations in the cell. Finally, combining eq 37, 38, and 43, we express the experimentally accessible quantity M_app as

$$M_\mathrm{app}^{-1} = K^{-1}c_\mathrm{p}^{-u}(1 + \alpha Kc_\mathrm{p}^{1+u})^2/(1 + \beta Kc_\mathrm{p}^{1+u}) \qquad (44)$$

When analyzing the experimental dependence of M_app on c_p, we will use a nonlinear least-squares fit to find the values of the four adjustable parameters: K, u, α, and β. Once these parameters are known, the molecular-weight averages of the original sample $\bar{M}_\mathrm{w}^\mathrm{or}$ and $\bar{M}_\mathrm{z}^\mathrm{or}$ may be calculated from the relations

$$\bar{M}_\mathrm{w}^\mathrm{or} = K\int_{r_\mathrm{m}}^{r_\mathrm{b}} c_\mathrm{p}^{1+u}r\,\mathrm{d}r \Big/ \int_{r_\mathrm{m}}^{r_\mathrm{b}} c_\mathrm{p}r\,\mathrm{d}r \qquad (45)$$

$$\bar{M}_\mathrm{z}^\mathrm{or} = K(1+u)\int_{r_\mathrm{m}}^{r_\mathrm{b}} c_\mathrm{p}^{1+2u}r\,\mathrm{d}r \Big/ \int_{r_\mathrm{m}}^{r_\mathrm{b}} c_\mathrm{p}^{1+u}r\,\mathrm{d}r \qquad (46)$$

The integrals in eq 45 and 46 are computed numerically from the experimental concentration profile. The polydispersity factor of the original sample u^or is given as

$$u^\mathrm{or} = \bar{M}_\mathrm{z}^\mathrm{or}/\bar{M}_\mathrm{w}^\mathrm{or} - 1 \qquad (47)$$

The second virial coefficient is calculated from eq 42. It is also convenient to introduce a new characteristic parameter β/α. Thus, our analysis produces four values for each sample: $\bar{M}_\mathrm{w}^\mathrm{or}$, u^or, A_2, and β/α.

Experimental Part

In this study we have reanalyzed the extensive experimental data on polystyrene in bromobenzene reported in our previous paper.[6] These experiments were performed on polystyrene samples with a rather narrow distribution of molecular weights (samples from Pressure Chemical Co.). As an example of polymers with a broader distribution function, we have analyzed the sedimentation equilibrium measurements on several samples of polyacrylamide (kindly provided by Dr. Chmelir, from Chem. Fabrik Stockhausen) in 0.2 M aqueous NaCl.[8] For these solutions, the value of v was found to be 0.687 mL/g.

Results and Discussion

As described in our previous papers,[4,5] we have evaluated the photographic plates from the sedimentation equilibria to obtain M_app and c_p at more than one hundred points in the cell. In this study we have tried to obtain from these data the four parameters of eq 44: K, u, α, β.

After many trials, we have developed the following computer algorithm and we used it for all experimental systems. 1. At the low-concentration end, the data were cut off at a concentration selected with respect to the appropriate refractive increment of the experimental system. This concentration (expressed as the shift of the

Table I
Results of Least-Squares Analysis of Sedimentation Equilibrium for Two Samples of Polystyrene in Bromobenzene

sample	col length, mm	photograph	$10^{-3}\overline{M}_w^{or}$	u^{or}	10^4A_2	β/α	r_{max}	Δ, %
7b	4.2	1	37.5	0.030	7.52	0.140	2.4	1.5[a]
		2	36.2	0.010	7.02	0.014	2.1	1.5[a]
		3	40.6	0.074	9.18	0.637	2.6	2.5
7b	11.5	1	37.5	0.023	7.47	0.080	11.0	1.0[a]
		2	36.7	0.014	7.43	0.070	10.5	1.0[a]
3b	4.0	1	433.8	0.092	4.14	0.190	15.0	1.1
		2	426.7	0.085	4.12	0.183	14.5	1.2
		3	417.5	0.076	4.11	0.182	14.0	1.2
3b	11.4	1	297.4	0.005	3.89	0.085	60.0	6.0
		2	309.0	0.018	3.88	0.089	62.0	7.0

[a] At concentrations less than 1 fringe, fluctuations up to 5% were observed.

Table II
Polystyrene in Bromobenzene: Comparison of Present and Older Results Based on the Same Experiments

	present results				older results			manufacturers' values	
sample	$10^{-3}\overline{M}_w^{or}$	u^{or}	10^4A_2	β/α	$10^{-3}\overline{M}_w^{or}$	u^{or}	10^4A_2	M	$\overline{M}_w/\overline{M}_n$
7b	37.3	0.025	7.54	0.08	35.9	0.010	6.38	37.0	<1.06
4b	114	0.000	5.43	0.13	116	0.015	5.08	110	<1.06
1c	182	0.000	4.69	0.06	184	0.015	4.43	200	<1.06
3b	426	0.084	4.12	0.18	392	0.07	3.17	390	<1.10
13a	830	0.24	4.16	0.39	702	0.17	2.97	670	<1.15
14b	1785[a]	0.58	2.77	0.15	2840	0.55	2.15	2000	<1.20

[a] $(\overline{M}_w/M_{app})_{max}$ value was 80; Δ was 3%.

interference fringe) was 100 μm for polystyrene in bromobenzene and 200 μm for polyacrylamide in 0.2 M aqueous NaCl. For our instrument, one fringe was about 300 μm. 2. The nonlinear least-squares fitting was applied to the quantity M_{app}^{-1}. 3. Each experimental point (at equal intervals along the radius of the cell) was given a statistical weight proportional to M_{app}. This choice gives about the same significance to each experimental point regardless of the shape of the M_{app} vs. c_p dependence. 4. Negative values of u were not allowed. 5. Neither were allowed the values of β/α, which were negative or which were larger than 0.9 (when the program tried to get $\beta/\alpha > 0.9$, this quantity was set equal to zero).

By analyzing a large number of computer results, we were able to formulate the rules governing the applicability of our method of calculation.

1. A good estimate of the concentration at the meniscus (bottom for polystyrene in bromobenzene) is imperative. Such a good estimate could be obtained only when the meniscus concentration was rather low (almost complete depletion at the meniscus).

2. Description of a relatively smooth function, as is M_{app}^{-1} vs. c_p, is always good when it is fitted to a function with four adjustable parameters. Accordingly, we had to establish a very rigid test of the fit. We describe the fit by means of the parameter $\Delta \equiv \delta M_{app}/M_{app}$, where δM_{app} is the difference between the experimental and fitted value of M_{app}. The value of Δ which we report is calculated for the point where it achieves its maximum value. Even in cases when the values of the parameters were grossly inadequate, Δ never exceeded 16%. In our experience, a good fit is represented by values of Δ about 1%; only occasionally were the values higher in the region of concentrations below one fringe. Experiments with $\Delta \sim 5\%$ are already inadequate; $\Delta > 8\%$ represents a failure of the fit.

3. The degree of nonideality of the sample proved to be an important parameter of the fit. We are describing it by the value $r_{max} = (\overline{M}_w/\overline{M}_{app})_{max}$, which is measured at the point of highest concentration. For $r_{max} < 2 \div 3$, the parameter β of eq 44 plays a negligible role and the computer program returns the value $\beta/\alpha = 0$. For $3 < r_{max} < 4 \div 5$, the role of β is small; the program returns erratic values of β/α. Within the range $5 < r_{max} < 25 \div 30$, the values of the parameters vary only a little. For $r_{max} > 30 \div 40$, eq 44 is no longer adequate; the value of Δ increases and the returned parameters are unreasonable ($\overline{M}_w^{or}$ is too low; also β/α is low).

4. The precision of the parameter u^{or} is ± 0.05 at best. For polymers with a very narrow distribution of molecular weights, $u = 0.0$ is frequently returned by the computer.

To illustrate these features, we present in Table I the results for two samples of polystyrene in bromobenzene. For each of the samples, two runs were analyzed: one in a short column, in which the concentration was moderate throughout the cell; the other in a long column, for which the concentrations went up to 0.07 g/mL. For the low molecular weight sample 7b the nonideality is still acceptable and both experiments yield the same values. The higher molecular weight sample 3b gives an acceptable fit in the short-column experiment; the too large nonideality in the long-column experiment leads to unreasonable results.

In Table II we have collected the results of those experiments on polystyrene in bromobenzene which were reasonable by the above standards. We compare the results with those obtained in our previous study[6] in which the method of evaluation was iterative and depended heavily on the behavior in the region of lowest concentration. The agreement for the lower molecular weight fractions is very good. The present method yields slightly higher molecular weight and polydispersity parameters for the higher molecular weight samples. Comparable results were also obtained when we reanalyzed the sedimentation equilibria of the same samples of polystyrene in benzene[5] and in mixed solvents.[7] In Figure 1, we present a typical dependence of M_{app}^{-1} vs. c_p for the highly nonideal sample 3b. In Table III are compiled the detailed results for two samples of polyacrylamide dissolved in 0.2 M aqueous NaCl; each sample was measured twice. Figure 2 represents a typical dependence of M_{app}^{-1} on concentration for this system. It is apparent from Table III that the fit is

Table III

Results of Least-Squares Analysis of Sedimentation Equilibrium for Two Samples of Polyacrylamide in 0.2 M NaCl

sample	run	photo-graph	$10^{-3}\overline{M}_w{}^{or}$	u^{or}	10^4A_2	β/α	r_{max}	Δ, %
W25499	1	1	585	0.58	3.11	0.00	3.0	3.0
		2	580	0.55	3.03	0.00	2.8	1.8
		3	578	0.55	3.03	0.00	2.8	4.0
	2	1	597	0.60	3.14	0.00	2.9	2.0
		2	631	0.68	3.50	0.27	3.1	1.3
		3	727	0.83	4.40	0.71	3.9	1.3
		4	650	0.62	3.33	0.14	3.4	2.2
W25655	1	1	2863	0.54	2.76	0.18	8.5	1.1
		2	2799	0.51	2.64	0.11	9.0	1.0
	2	1	2728	0.59	2.91	0.27	8.0	0.4
		2	2750	0.51	2.84	0.23	8.0	0.7
		3	2513	0.41	2.75	0.20	6.5	1.0

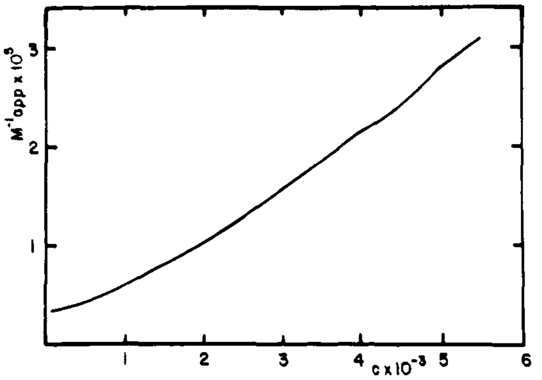

Figure 1. Dependence of $M_{app}{}^{-1}$ on concentration (expressed as the shift of the interference fringe in μm) for polystyrene sample 3b in bromobenzene. Column length 4.0 mm, photograph 1. On the scale of the plot, the experimental dependence and the fitted one are indistinguishable.

usually very good. As the nonideality of our polyacrylamide solutions is not extreme, the results seem to be significant even for samples with molecular weight in the region of millions. While we cannot compare our data on polyacrylamide with any other measurement, we find that the values of the polydispersity parameter u^{or} are quite reasonable for an unfractionated polymer. Also the values of the second virial coefficient A_2 and their relation to molecular weight are rather reasonable.

It is obvious from Tables I and III that there is an appreciable scatter of values obtained from different photographs (some of them taken immediately after each other). This scatter is probably related to the fact that we are extracting too many parameters (four) from a smooth dependence. However, the data averaged for all photographs (Table II) seem to be much more reliable.

Conclusions

In the theoretical part we have designed a method of the analysis of the sedimentation equilibria of polymers in highly nonideal solutions. The method is based on the assumption that (1) the distribution of molecular weights of the polymer sample is described reasonably well by the Schulz–Zimm distribution function (eq 20) and (2) the nonideality of the solution follows eq 41.

Despite the crudeness of these assumptions, the method yielded plausible results both for highly nonideal solutions of polymers with a narrow distribution of molecular weights and for unfractionated samples with a broader distribution.

The fit between the experimental dependence and the fitted one gets worse when the nonideality of the solution exceeds the limit of the applicability of the method.

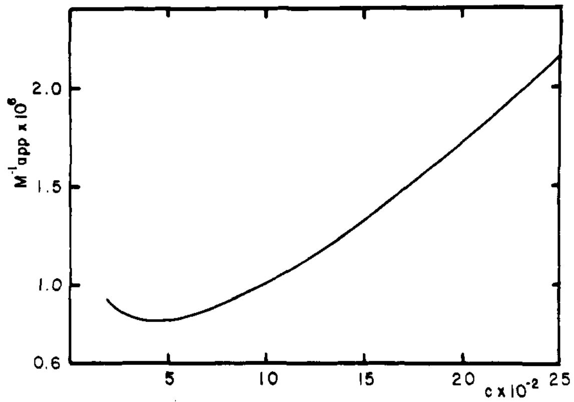

Figure 2. Dependence of $M_{app}{}^{-1}$ on concentration (expressed as the shift of the interference fringe in μm) for polyacrylamide sample W25655 (run 2, photograph 2). On the scale of the plot, the experimental dependence and the fitted one are indistinguishable.

Similarly, we got a poor fit when we tried to analyze a mixture of two narrow fractions (i.e., the sample with bimodal distribution). We find this feature very convenient: *a poor fit warns us that the assumptions of the method have been violated and that the results are not significant.* Of course, it is also possible that some samples with a broad unknown distribution of molecular weights in a nonideal solution may give a good fit and still yield incorrect results. On the other hand, a reasonable estimate of the *type* of the distribution may be usually made if the origin and/or history of the sample is known.

In summary, the method yields simultaneously reasonable values of molecular weight, polydispersity, and second virial coefficient, provided that the distribution of molecular weights can be reasonably described by the Schulz–Zimm distribution function and that the conditions of the experiment were selected as not to go into the region of extreme nonideality.

Acknowledgment. The author is grateful to The Robert A. Welch Foundation (Grant F-563) for financial support of this study.

References and Notes

(1) Th. G. Scholte, *J. Polym. Sci., Part A-2*, **6**, 91, 111 (1968).
(2) Th. G. Scholte, *Eur. Polym. J.*, **6**, 51 (1970).
(3) P. J. Wan and E. T. Adams, Jr., *Biophys. Chem.*, **5**, 207 (1976).
(4) P. Munk and M. E. Halbrook, *Macromolecules*, **9**, 568 (1976).
(5) S. G. Chu and P. Munk, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1163 (1977).
(6) S. G. Chu and P. Munk, *Macromolecules*, **11**, 101 (1978).
(7) S. G. Chu and P. Munk, *Macromolecules*, **11**, 879 (1978).
(8) P. Munk, T. M. Aminabhavi, P. Williams, D. B. Hoffman, and M. Chmelir, *Macromolecules*, **13**, 871 (1980).