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Fractionation of a Polydisperse Polymer Using an Anti-Solvent: Application of Continuous Thermodynamics

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Fractionation of a Polydisperse Polymer Using an Anti-Solvent. Application of Continuous Thermodynamics

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Abstract

Continuous thermodynamics is used to calculate liquid-liquid equilibria in a ternary system containing polydisperse polymer, one good solvent and one poor solvent (anti-solvent). The polymer has a semi-infinite molecular-weight distribution which can be described by a gamma distribution. From Flory-Huggins theory, the logarithm of the distribution ratio of the polymer is a linear function of the molecular weight. Because the distribution of polymer between the two liquid phases is very sensitive to binary Flory parameters, the Flory parameters must be fitted to the ternary data. Results are given for the system benzene, ethanol and polydisperse polystyrene.

Introduction

A classical method for fractionating a polydisperse polymer is to dissolve the polymer completely in a good solvent and then, progressively, to add small amounts of a poor solvent (anti-solvent). The high-molecular-weight polymer precipitates first. As more anti-solvent is added, progressively lower-molecular-weight polymer precipitates.

To obtain quantitative representation of fractionation, we require a model for the thermodynamic properties of the polymer / solvent / anti-solvent system and we must specify the original molecular-weight distribution.

Continuous thermodynamics provides a useful tool for fractionation calculations. When compared to the pseudo-component method, continuous thermodynamics has two advantages: computer-time requirements are often reduced and, more important, ambiguous results, based on arbitrary definition of pseudo-components, are avoided.[1,2,3,4,5]

Cotterman and Prausnitz applied continuous thermodynamics and Flory-Huggins theory to calculate the effect of temperature on equilibria in a system containing one polymer and one solvent.[6] Continuous thermodynamics has also been applied to calculate phase behavior in the high-pressure ethylene-polyethylene system by Rätzsch and Kehlen,[5,7] and by Sako *et al.*[8] The purpose of this paper is to show that continuous thermodynamics provides a useful tool for describing phase equilibria in a system containing one polymer and two solvents.

Theory

We consider two equilibrated liquid phases, containing one good solvent*(1)*, one poor solvent*(2)*, and one polydisperse polymer*(3)*. For every component, the activity in phase ′ is equal to that in phase ″:

$$a_1' = a_1'' \tag{1}$$

$$a_2' = a_2'' \tag{2}$$

$$a_3'\,(J) = a_3''\,(J) \tag{3}$$

where ′ and ″ denote the precipitate and the supernatant phase, respectively. At constant temperature, all activities depend on concentration but, in addition, the activity of the polymer is a function of molecular weight, J.

We use the Flory-Huggins theory of polymer solutions. As shown in the Appendix, the activities are given by

$$\ln a_1 = \ln \Phi_1 + (\Phi_2+\Phi_3^T) - \frac{\Phi_2}{m_2} - \frac{\Phi_3^T}{\bar{m}_3} + \left(\chi_{12}\,\Phi_2 + \chi_{13}\,\Phi_3^T\right)\cdot(\Phi_2+\Phi_3^T) - \chi_{23}\cdot\frac{\Phi_2}{m_2}\cdot\Phi_3^T \tag{4}$$

$$\ln a_2 = \ln \Phi_2 + (\Phi_1+\Phi_3^T) - \Phi_1\,m_2 - m_2\cdot\frac{\Phi_3^T}{\bar{m}_3} + \left(\chi_{12}\,m_2\,\Phi_1 + \chi_{23}\,\Phi_3^T\right)\cdot(\Phi_1+\Phi_3^T) - \chi_{13}\cdot\Phi_1\cdot m_2\cdot\Phi_3^T \tag{5}$$

$$\ln a_3(J) = \ln \Phi_3(J) + 1 - \Phi_1\,m_3(J) - \frac{\Phi_2}{m_2}\cdot m_3(J) - m_3(J)\cdot\frac{\Phi_3^T}{\bar{m}_3} + \left(\chi_{13}\,\Phi_1\,m_3(J) + \chi_{23}\,\Phi_2\,\frac{m_3(J)}{m_2}\right)\cdot(\Phi_1+\Phi_2) - \chi_{12}\cdot\Phi_1\cdot\Phi_2\cdot m_3(J) \tag{6}$$

where χ is the Flory parameter, Φ is the volume fraction, and m is the molar-volume ratio of a given species to that of solvent *1*. For the polymer, volume fraction and molar-volume ratio are functions of molecular weight, J. Total volume fraction of the polymer is denoted by $\Phi_3{}^T$. We assume that Flory parameters χ_{13} and χ_{23} are independent of J.

The distribution factor K_i is defined as the ratio $\Phi_i{}' \,/\, \Phi_i{}''$. From Equations (4)-(6), we obtain

$$\begin{aligned}\ln K_1 &\equiv \ln \left(\frac{\Phi_1{}'}{\Phi_1{}''}\right)\\ &= -\sigma + 2\,\chi_{13}\cdot\left(\Phi_1{}'-\Phi_1{}''\right) + \left(\Phi_2{}'-\Phi_2{}''\right)\cdot\left(\chi_{13} - \chi_{12} + \frac{\chi_{23}}{m_2}\right)\end{aligned} \tag{7}$$

$$\begin{aligned}\ln K_2 &\equiv \ln \left(\frac{\Phi_2{}'}{\Phi_2{}''}\right)\\ &= m_2\cdot\left[-\sigma + 2\,\frac{\chi_{23}}{m_2}\cdot\left(\Phi_2{}'-\Phi_2{}''\right)\right.\\ &\qquad \left. + \left(\Phi_1{}'-\Phi_1{}''\right)\cdot\left(\chi_{13} - \chi_{12} + \frac{\chi_{23}}{m_2}\right)\right]\end{aligned} \tag{8}$$

$$\ln K_3(J) \equiv \ln \left(\frac{\Phi_3{}'(J)}{\Phi_3{}''(J)}\right) = -\, m_3(J)\cdot\sigma \tag{9}$$

$$\begin{aligned}\sigma = {} & (1-\chi_{13})\cdot(\Phi_1{}''-\Phi_1{}') + (1-\chi_{23})\cdot\frac{(\Phi_2{}''-\Phi_2{}')}{m_2}\\ & - \frac{(1-\Phi_1{}'-\Phi_2{}')}{\overline{m_3}{}'} + \frac{(1-\Phi_1{}''-\Phi_2{}'')}{\overline{m_3}{}''}\\ & - \chi_{12}\,\Phi_1{}'\,\Phi_2{}' - \chi_{13}\cdot\Phi_1{}'\cdot(1-\Phi_1{}'-\Phi_2{}') - \chi_{23}\cdot\frac{\Phi_2{}'}{m_2}\cdot(1-\Phi_1{}'-\Phi_2{}')\\ & + \chi_{12}\,\Phi_1{}''\,\Phi_2{}'' + \chi_{13}\cdot\Phi_1{}''\cdot(1-\Phi_1{}''-\Phi_2{}'')\\ & + \chi_{23}\cdot\frac{\Phi_2{}''}{m_2}\cdot(1-\Phi_1{}''-\Phi_2{}'')\end{aligned} \tag{10}$$

From material balance, feed composition $\Phi_i{}^F$ is related to $\Phi_i{}'$ and $\Phi_i{}''$ by

$$\Phi_1{}^F = \Phi_1{}'\left(\frac{V_L{}'}{V_F}\right) + \Phi_1{}''\left(1 - \frac{V_L{}'}{V_F}\right) \tag{11}$$

$$\Phi_2^F = \Phi_2' \left(\frac{V_L'}{V_F} \right) + \Phi_2'' \left(1 - \frac{V_L'}{V_F} \right) \tag{12}$$

$$\Phi_3^F (J) = \Phi_3' (J) \left(\frac{V_L'}{V_F} \right) + \Phi_3'' (J) \left(1 - \frac{V_L'}{V_F} \right) \tag{13}$$

Application to a Real System

To illustrate the use of these equations, we consider the system benzene*(1)*, ethanol*(2)*, and polydisperse polystyrene*(3)* at 38.6 °C. Experimental data for this system were reported by Breitenbach and Wolf.[9] We have preformed a flash calculation for the case where the volume fraction of polystyrene in the feed is 0.0027 and where the volumetric ratio of benzene to ethanol is 2:1, From molar-volume data for benzene and ethanol,[10] and from partial-specific-volume data for polystyrene,[11] the molar-volume ratios m_2 and $m_3(J)$ are given by

$$m_2 = 0.656$$

$$m_3(J) = 0.0101 \cdot J$$

The mass distribution of polymer molecular weight given by Breitenbach and Wolf is semi-infinite,[9] starting at zero molecular weight, a mean of 2.19×10^5, and a variance of 2.46×10^{10}. We fit this mass distribution with a gamma distribution $F(J)$ of the form

$$F(J) = \frac{\left(\frac{J - \gamma}{\beta} \right)^{\alpha - 1}}{\beta \, \Gamma(\alpha)} \exp \left(- \frac{J - \gamma}{\beta} \right)$$

where α, β and γ are adjustable parameters, and $\Gamma(\alpha)$ is the gamma function of α. For gamma distribution, the mean and variance are given by $\alpha\beta + \gamma$ and $\alpha\beta^2$, respectively, and the starting point is γ. From the mass distribution of polymer, we obtain $\alpha = 1.95$, $\beta = 1.12 \times 10^5$, and $\gamma = 0$.

For the three binary systems, we use the Flory parameters

$$\chi_{12} = 1.739$$

$$\chi_{13} = 0.2210$$

$$\chi_{23} = 1.451$$

The flash calculation shows that the volumetric ratio of polymer in the supernatant phase to that in the precipitate phase is 1.002. The volumetric ratio of supernatant phase to the feed, f_s, is 0.967. In comparison, the experimental result shows that the volumetric ratio of polymer in the supernatant phase to that in the precipitate phase is 1.038; and the volumetric ratio of supernatant phase to the feed, f_s, is 0.993.

From Equation (9), we obtain an expression for the volumetric ratio of polymer in the supernatant phase to that in the precipitate phase, $M_p(J)$, as a function of polymer molecular weight J:

$$\begin{aligned}\ln\left[M_p(J)\right] &= \ln\left[\frac{f_s \cdot \Phi_3'(J)}{(1-f_s)\cdot\Phi_3''(J)}\right] \\ &= \ln\left[\frac{f_s}{(1-f_s)}\right] + \ln\left[\frac{\Phi_3'(J)}{\Phi_3''(J)}\right] \\ &= \ln\left[\frac{f_s}{(1-f_s)}\right] + \ln\left[K_3(J)\right] \\ &= \ln\left[\frac{f_s}{(1-f_s)}\right] - m_3(J)\cdot\sigma \qquad (14)\end{aligned}$$

In Equation (14), the only dependence on polymer molecular weight, J, is the linear dependence of $m_3(J)$ on J. Therefore, as shown in Figure 1, there is a linear relationship between ln $[M_p(J)]$ and polymer molecular weight J.

Figure 2 shows the distributions of polystyrene in the feed, precipitate phase, and supernatant phase.

The flash calculations are very sensitive to the values used for Flory parameters. Figure 1 shows the effect on distribution of polymer between the two phases when each χ is set higher by 1%. Calculated results are particularly sensitive to Flory parameter χ_{23}.

The Flory parameters used in this calculation provide the best fit for the experimental fractionation data. From Scatchard-Hildebrand theory, Flory parameter χ is related to solubility parameter δ by

$$\chi_{ab} = \frac{v_a}{RT}\cdot(\delta_a-\delta_b)^2 \qquad (15)$$

where v_a is molar volume of (solvent) component a. Using Equation (15) and tabulated solubility parameters,[10] χ_{12}, χ_{13} and χ_{23} are 2.13, 0.0015 and 1.47, respectively.

For the binary system ethanol and polystyrene, there is good agreement between the best-fit parameter and that calculated from Scatchard-Hildebrand theory.

For the binary system benzene and polystyrene, the reported experimental values of χ_{13} range from 0.19 to 0.46.[12] This range includes the value that was used in the flash calculation (χ_{13}=0.2210). The result from solubility-parameter calculations (0.0015) is clearly too low.

For the binary system benzene and ethanol, we used experimental vapor-liquid data reported by Udovenko at 40 °C.[13] We used a constant χ_{12} for the entire concentration region and found χ_{12}=2.24 to be the best fit.[†] This χ_{12} value is much higher than the one used to correlate the ternary data. Clearly, for ternary systems, Flory parameters must be fitted to the ternary data.

Conclusion

Continuous thermodynamics provides a convenient method for calculating liquid-liquid equilibria in a ternary system containing polydisperse polymer, one good solvent and one poor solvent (anti-solvent). When Flory-Huggins theory is used to describe the Gibbs energy of mixing, it follows that the logarithm of the distribution ratio of the polymer is a linear function of the molecular weight, in agreement with experiment. Since the calculations are very sensitive to binary Flory parameters, calculated ternary results must unfortunately be fitted to a few ternary data; quantitative predictions from binary data alone are not accurate.

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[†] For the molar-volume ratio in this binary system (m_2=0.656), the two components are completely miscible when $\chi_{12} \leq 2.50$.

Appendix: Derivations of Equations (4) - (6)

We consider a system containing one good solvent *(1)*, one poor solvent *(1)*, and a polydisperse polymer *(i = 3, 4, 5, ...)* where i denotes polymer molecules of the same chemical composition but different molecular weights.

From Flory-Huggins theory, the Gibbs energy of mixing is given by[14, 15]

$$\Delta G_{mix} = kT \left[n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \sum_{i=3} n_i \ln \Phi_i \right.$$
$$+ \chi_{12}\, n_1\, \Phi_2 + \sum_{i=3} \chi_{1i}\, n_1\, \Phi_i + \sum_{i=3} \chi_{2i}\, n_2\, \Phi_i$$
$$\left. + \sum_{i=3} \sum_{\substack{j=3 \\ j \neq i}} \chi_{ij}\, n_i\, \Phi_j \right] \tag{A-1}$$

where n is the number of molecules, k is Boltzmann's constant, and T is temperature. Because components *(3)*, *(4)*, *(5)*, ... are chemically the same, we have

$$\chi_{ij} = 0$$
$$\chi_{1i} = \chi_{1j}$$
$$\chi_{2i} = \chi_{2j}$$

where i, j = 3, 4, ...

Equation (A-1) becomes

$$\Delta G_{mix} = kT \left[n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \sum_{i=1} n_{3i} \ln \Phi_{3i} \right.$$
$$\left. + \chi_{12}\, n_1\, \Phi_2 + \chi_{13}\, n_1 \left(\sum_{i=1} \Phi_{3i} \right) + \chi_{23}\, n_2 \left(\sum_{i=1} \Phi_{3i} \right) \right] \tag{A-2}$$

In Equation (A-2), $3i$ $(i = 1, 2, 3, \ldots)$ denotes polymer molecules of different molecular weights.

Activities a and chemical potentials μ are related to ΔG_{mix} by

$$RT \ln a_1 = \left(\mu_1 - \mu_1^0 \right) = N_{AV} \left(\frac{\partial\, \Delta G_{mix}}{\partial\, n_1} \right)_{T,\, P,\, n_2,\, n_{3i}} \tag{A-3}$$

$$RT \ln a_2 = \left(\mu_2 - \mu_2^0\right) = N_{AV} \left(\frac{\partial \ \Delta G_{mix}}{\partial n_2}\right)_{T,\,P,\,n_1,\,n_{3i}} \tag{A-4}$$

$$RT \ln a_{3j} = \left(\mu_{3j} - \mu_{3j}^0\right) = N_{AV} \left(\frac{\partial \ \Delta G_{mix}}{\partial n_{3j}}\right)_{T,\,P,\,n_1,\,n_2,\,n_{3i,\,3i \neq 3j}} \tag{A-5}$$

where N_{AV} is Avogadro's number.

Volume fraction Φ and number of molecules n are related by

$$\Phi_1 = \frac{n_1}{\left(n_1 + n_2 m_2 + \sum_{i=1} n_{3i} m_{3i}\right)} \tag{A-6}$$

$$\Phi_2 = \frac{n_2 m_2}{\left(n_1 + n_2 m_2 + \sum_{i=1} n_{3i} m_{3i}\right)} \tag{A-7}$$

$$\Phi_{3i} = \frac{n_{3i} m_{3i}}{\left(n_1 + n_2 m_2 + \sum_{i=1} n_{3i} m_{3i}\right)} \tag{A-8}$$

where m is the molar-volume ratio of a given species to that of solvent *1*. The number average of m_{3i} is given by

$$\overline{m_3} = \frac{\sum_{i=1} m_{3i} n_{3i}}{\sum_{i=1} n_{3i}} \tag{A-9}$$

Combining Equations (A-2) - (A-9), we obtain expressions for the activities

$$\ln a_1 = \ln \Phi_1 + (\Phi_2 + \Phi_3^T) - \frac{\Phi_2}{m_2} - \frac{\Phi_3^T}{\overline{m_3}} \tag{A-10}$$

$$+ \left(\chi_{12}\,\Phi_2 + \chi_{13}\,\Phi_3^T\right) \cdot (\Phi_2 + \Phi_3^T) - \chi_{23} \cdot \frac{\Phi_2}{m_2} \cdot \Phi_3^T$$

$$\ln a_2 = \ln \Phi_2 + (\Phi_1+\Phi_3^T) - \Phi_1\, m_2 - m_2 \cdot \frac{\Phi_3^T}{\overline{m_3}} \tag{A-11}$$

$$+ \left(\chi_{12}\, m_2\, \Phi_1 + \chi_{23}\, \Phi_3^T \right) \cdot (\Phi_1+\Phi_3^T) - \chi_{13} \cdot \Phi_1 \cdot m_2 \cdot \Phi_3^T$$

$$\ln a_{3i} = \ln \Phi_{3i} + 1 - \Phi_1\, m_{3i} - \frac{\Phi_2}{m_2} \cdot m_{3i} - m_{3i} \cdot \frac{\Phi_3^T}{\overline{m_3}} \tag{A-12}$$

$$+ \left(\chi_{13}\, \Phi_1\, m_{3i} + \chi_{23}\, \Phi_2\, \frac{m_{3i}}{m_2} \right) \cdot (\Phi_1+\Phi_2)$$

$$- \chi_{12} \cdot \Phi_1 \cdot \Phi_2 \cdot m_{3i}$$

where total volume fraction of the polymer is given by

$$\Phi_3{}^T = \sum_{i=1} \Phi_{3i} \tag{A-13}$$

NOTATION

Upper case

J	molecular weight of a polymer molecule
K_i	distribution factor (ratio of volume fraction in the supernatant phase to that in the precipitate phase for species i)
$K_3(J)$	distribution factor of polymer with molecular weight J
$M_p(J)$	distribution ratio (volumetric ratio of polymer in the supernatant phase to that in the precipitate phase as a function of J)
R	gas constant
T	absolute temperature

Lower case

a	activity
f_s	volumetric ratio of supernatant phase to the feed
k	Boltzmann's constant (used in the Appendix)
m_2	molar-volume ratio of solvent *2* to solvent *1*
$m_3(J)$	molar-volume ratio of the polymer with molecular weight J to solvent *1*
$\overline{m_3}$	number average of $m_3(I)$
v	molar volume

Greek symbols

α,β,γ	parameters for gamma distribution
δ	solubility parameter
Φ_i	volume fraction of species i
$\Phi_3(J)$	volume fraction of polymer with molecular weight J
Φ_3^T	total volume fraction of the polydisperse polymer
μ	chemical potential
χ_{ij}	Flory parameter for ij binary

Subscripts and superscripts

subscripts

1	good solvent for the polymer
2	poor solvent for the polymer
3	polymer
a,b	integer numbers refer to component a,b

superscripts

F	feed
$'$	supernatant phase
$''$	precipitate phase

References

1. R. L. Cotterman, R. Bender, and J. M. Prausnitz, ''Phase Equilibria for Mixtures Containing Very Many Components. Development and Application of Continuous Thermodynamics for Chemical Process Design,'' *Ind. Eng. Chem. Process Des. Dev.*, **24**, 194 (1985).

2. R. L. Cotterman and J. M. Prausnitz, ''Flash Calculations for Continuous or Semicontinuous Mixtires Using an Equation of State,'' *Ind. Eng. Chem. Process Des. Dev.*, **24**, 434 (1985).

3. R. L. Cotterman, G. F. Chou, and J. M. Prausnitz, ''Comments on 'Flash Calculations for Continuous or Semicontinuous Mixtures Using an Equation of State','' *Ind. Eng. Chem. Process Des. Dev.*, **25**, 840 (1986).

4. H. Kehlen and M. T. Rätzsch, ''Liquid-Liquid Phase Separation in Polymer Systems and Polymer Compatibility by Continuous Thermodynamics,'' *Z. Physik. Chem., Leipzig*, **264**, 1153 (1983).

5. M. T. Rätzsch and H. Kehlen, ''Continuous Thermodynamics of Polymer Solutions: The Effect of Polydispersity on the Liquid-Liquid Equilibrium,'' *J. Macromol. Sci. - Chem.*, **A22(3)**, 323 (1985).

6. R. L. Cotterman, Phase Equilibria for Complex Fluid Mixtures at High Pressures. Development and Application of Continuous Thermodynamics, Ph.D. Dissertation, University of California, Berkeley (1985).

7. H. Kehlen and M. T. Rätzsch, ''Phase Equilibria in Systems with Polymer Components Treated by Continuous Thermodynamics,'' *Wiss. Z. Tech. Hochsch. "Carl Schorlemmer" Leuna-Merseburg*, **29**, 326 (1987).

8. T. Sako, A. H. Wu, and J. M. Prausnitz, ''A Cubic Equation of State for High-Pressure Phase Equilibria of Mixtures Containing Polymers and Volatile Fluids,'' submitted to *J. of App. Polym. Sci.* (May 1988).

9. J. W. Breitenbach and B. A. Wolf, ''Untersuchungen von Phasengleichgewichten an Polymerlösungen mittels Säulenfraktionierung,'' *Makromol. Chem.*, **108**, 263 (1967).

10. C. Hansen, ''Solubility Parameters,'' in *Encyclopedia of Chemical Technology, 2nd Ed.*, **Supplement**, 889, John Wiley & Sons, New York (1963).

11. R. H. Boundy and R. F. Boyer, "Styrene: Its Polymers, Copolymers and Derivatives," Am. Chem. Soc. Monograph Series, Reinhold Pub. Corp., New York, NY (1952).

12. C. J. Sheehan and A. L. Bisio, "Polymer / Solvent Interaction Parameters," *Rubber Chem. Technol.*, **39**, 149 (1966).

13. V. V. Udovenko and L. G. Fatkulina, *Zh. Fiz. Khim.*, **26**, 719 (1952).

14. J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd ed.*, Prentice-Hall, New Jersey (1986).

15. P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, New York (1953).

Figure 1. Distribution of polystyrene between the supernatant phase and the precipitate phase

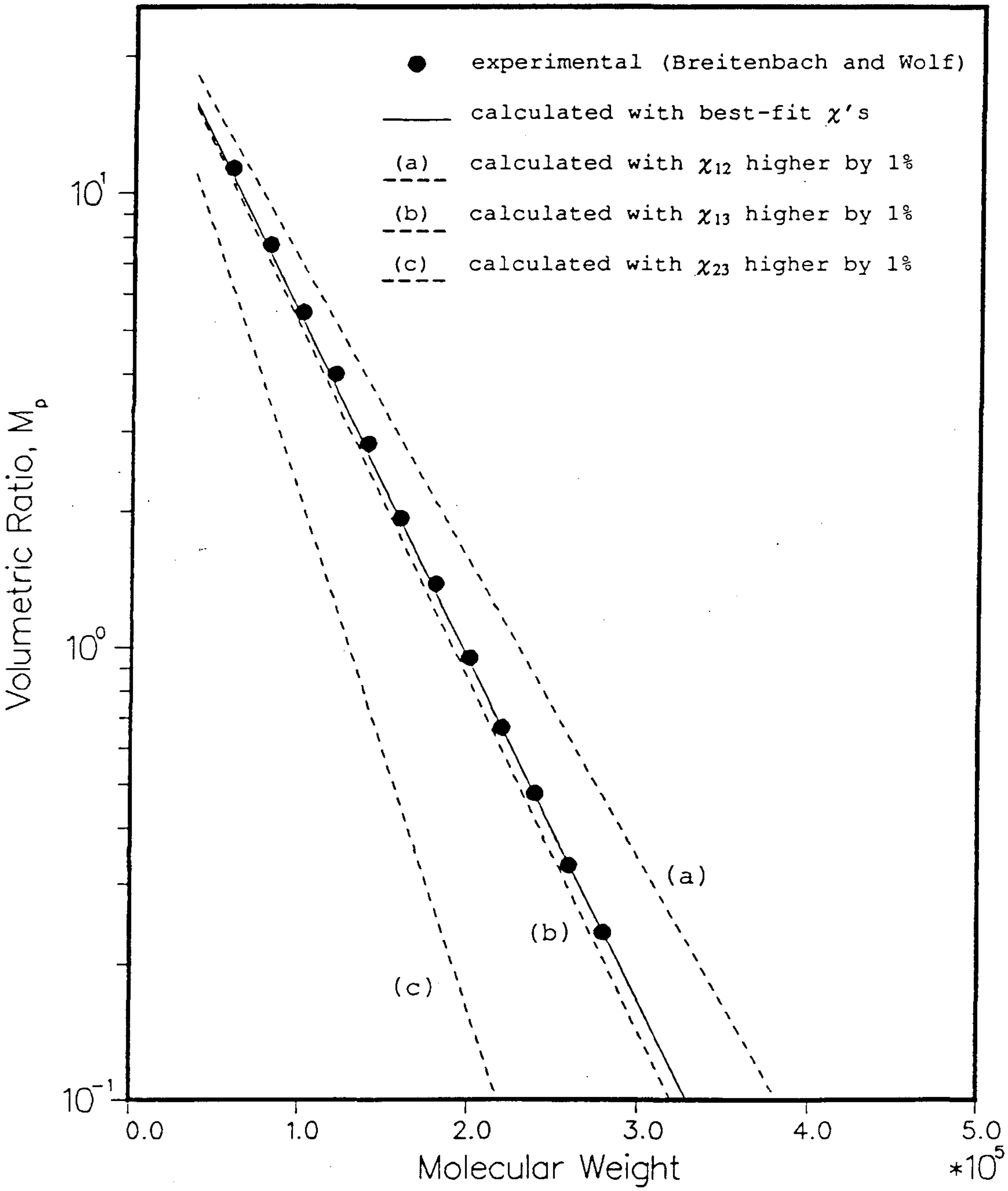
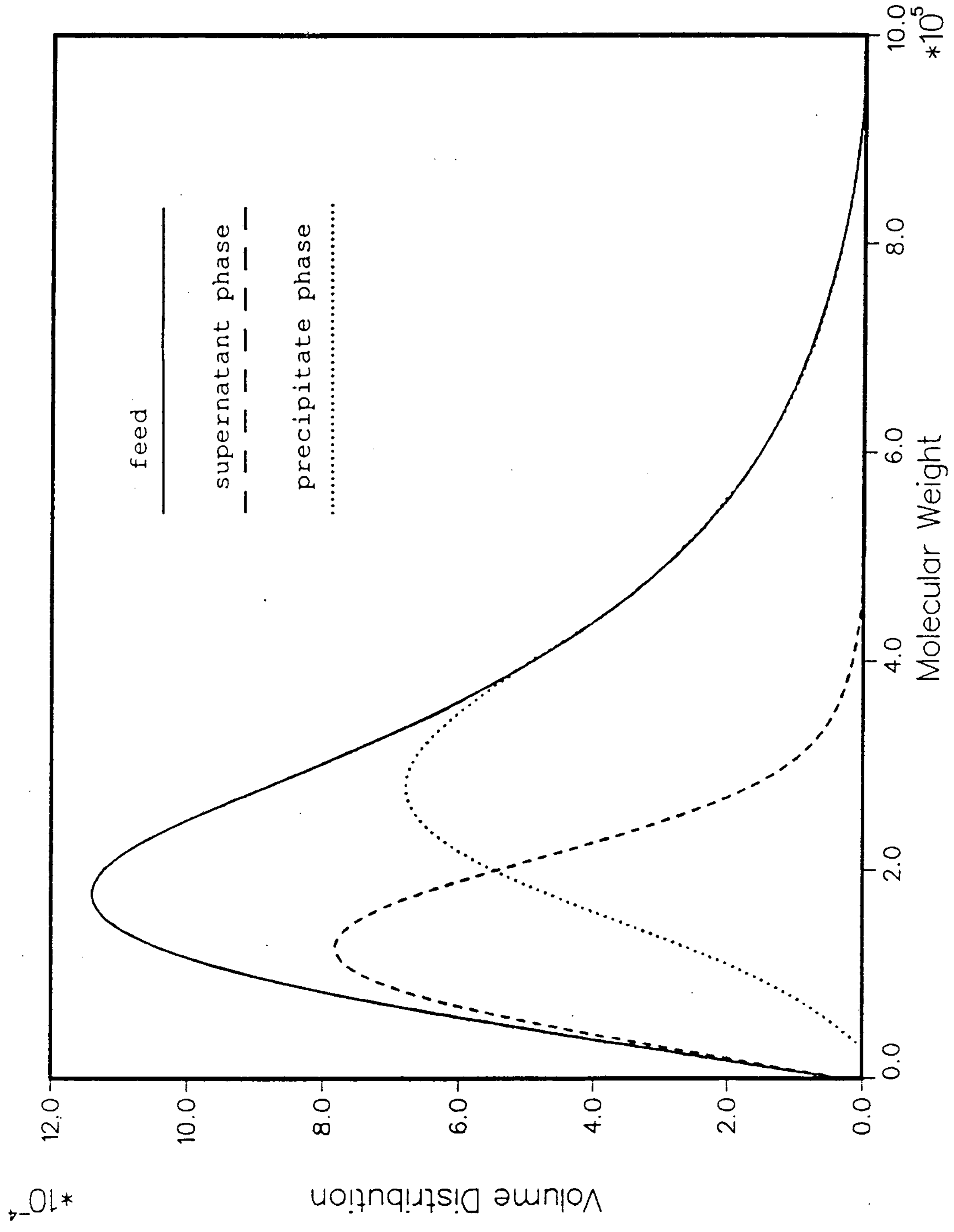


Figure 2. Volume distributions of polydisperse polystyrene



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