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## **SIMULATION OF BAKER-WILLIAMS FRACTIONATION BY CONTINUOUS THERMODYNAMICS**

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### **ABSTRACT**

Based on continuous thermodynamics and its application to the theory of successive polymer fractionation procedures, a theory of column fractionation is developed. In continuous thermodynamics the polydispersity of polymers is accounted for by the direct use of the continuous distribution function in the thermodynamic equations. In this way equations which are favorable for computer simulations are obtained. As an example, Baker-Williams fractionation is chosen for presenting theory and computer simulation. The generalization to other column fractionations based on solubility differences is easily possible.

### **INTRODUCTION**

Precipitation fractionation as developed by Baker and Williams [1] is one of the best known column fractionation procedures. The fractionation is performed in a glass-bead filled column with a temperature gradient down the column. To start the fractionation, the total polymer is precipitated on the glass beads of a section at the entry of the column (or in a separate vessel). In a mixing vessel a nonsolvent and a solvent are mixed to form a mixture with progressively more solvent power through

continuous enrichment of the solvent. The polymer is dissolved by adding the solvent mixture. The resulting sol phase moves relatively slowly in the column, and the polymer in a given increment of the liquid sol stream becomes less soluble due to the temperature gradient and precipitates partially on the glass beads as a gel phase. The fractionation is achieved by the repeated exchange of polymer molecules between the stationary gel phase and the mobile sol phase. The superposition of a solvent/nonsolvent gradient and a temperature gradient leads to a very high separation efficiency.

There are some papers dealing with the theory of precipitation fractionation [2-5]. They give an explanation of some experimental effects. However, the authors consider only one or two polymer species. In the present work the polydispersity of the polymer will be fully accounted for by direct use of the continuous molecular weight distribution.

The treatment will be based on a model subdividing the column into stages and the solution stream into parts with equal volumes. Hence, the column fractionation will be considered as a combination of many local liquid-liquid equilibria and treated in an analogous way as successive fractionation procedures. The problem is the mathematical and computer treatment of such a large number of connected equilibria. The application of continuous thermodynamics to successive fractionation procedures presented earlier [6] resulted in a lucid structure of the corresponding equations. These equations form the basis for theory and computer simulation of the Baker-Williams fractionation.

## MODEL

At first a model is needed for describing the column fractionation by a number of local equilibria. In this paper a model is used similar to that by Smith [5]. The column is subdivided into stages labeled with  $m$  ( $m = 0, 1, 2, \dots$ ). The liquid stream is also subdivided into increments with equal volumes, labeled with  $n$  ( $n = 0, 1, 2, \dots$ ). At time zero the volume increment  $n = 0$  fills stage  $m = 0$ , at time one the volume increment  $n = 0$  occupies stage  $m = 1$  and the volume increment  $n = 1$  occupies stage  $m = 0$ , etc. Each volume increment  $n$  at each stage  $m$  is considered to form a liquid-liquid equilibrium ( $nm$ ) between the sol phase ' and the gel phase ". The gel phases ", which are coated on the surfaces of the small glass beads, are stationary, i.e., they remain at the same stage  $m$  during the progress of time. However, the moving sol phases ' always remain in the same volume increment  $n$ .

Starting the fractionation the total polymer is assumed to be precipitated at stage  $m = m_p = 0$  or to be distributed evenly among the  $m_p + 1$  stages from  $m = 0$  to  $m = m_p$ . The temperature gradient is expressed by

$$\begin{aligned} T_m &= T_0; & m &\leq m_p \\ T_m &= T_0 - (m - m_p)\Delta T; & m &> m_p \end{aligned} \quad (1)$$

Here  $T_m$  is the temperature of stage  $m$  and  $\Delta T$  is the constant temperature difference between neighboring stages. The segment fraction  $Y$  of the solvent in the solvent/nonsolvent mixture supplied to the entry (\*) of the column,  $Y_{n0}^*$ , is assumed to be given by

$$Y_{n0}^* = Y_{00}^* + \Delta Y^*[1 - \exp(-n/n^*)] \quad (2)$$

where  $Y_{00}^*$ ,  $\Delta Y^*$ , and  $n^*$  are the parameters of the function. The polymer fractions are obtained from the sol phases ' of the last stage.

### PHASE EQUILIBRIUM

The theoretical basis of the polymer distribution between two phases is formed by the thermodynamics of the liquid-liquid equilibrium (LLE) of polymer solutions. Detailed treatments by continuous thermodynamics [7, 8] and its application to successive polymer fractionation [6] were presented earlier. In the present paper the nomenclature and the equations describing phase equilibria conform to [6] with some enlargements resulting from the presence of the second solvent. Therefore, only the most important equations will be summarized.

A solution of a solvent A, a nonsolvent B, and a polydisperse polymer C is considered. The individual species of the polymer C are identified by their segment numbers  $r$ . The essence of continuous thermodynamics consists in considering  $r$  as a continuously variable quantity. The composition of the polymer is described by the segment molar distribution function  $W(r)$ , i.e.,  $W(r)dr$  equals the segment fraction of all polymer species with segment numbers between  $r$  and  $r + dr$ . If  $r_0$  is the smallest and  $r^0$  the largest occurring segment number of polymer molecules, the normalization relation reads

$$\int W(r)dr = 1, \quad \int = \int_{r_0}^{r^0} \quad (3)$$

The number-average segment number ( $\bar{r}$ ) of a considered phase is given by

$$\frac{1}{\bar{r}} = \frac{Y(1 - \psi)}{r_A} + \frac{(1 - Y)(1 - \psi)}{r_B} + \frac{\psi}{r_C}$$

$$\frac{1}{\bar{r}_C} = \int \frac{W(r)}{r} dr \quad (4)$$

where  $\psi$  is the overall segment fraction of the polymer in this phase,  $Y(1 - \psi)$  is the segment fraction of the solvent, and  $(1 - Y)(1 - \psi)$  is the segment fraction of the nonsolvent.

The equations describing the phase equilibrium are obtained by combining the equilibrium conditions with the material balances. Continuous thermodynamics of the LLE results in simple relations interrelating the distribution functions of the polymer in the two coexisting phases ' and '' and in the feed-phase  $F$  [6]:

$$\psi' W'(r) = \frac{1 - K(r)}{1 - \phi} \psi^F W^F(r) \quad (5)$$

$$\psi'' W''(r) = \frac{K(r)}{\phi} \psi^F W^F(r) \quad (6)$$

$\phi$  gives the fraction of the overall amount of segments in the feed that forms phase '', and  $K$  is the precipitation rate:

$$K(r) = \frac{\phi}{\phi + (1 - \phi) \exp[-r\rho_C(r)]} \quad (7)$$

with

$$\rho_C(r) = \frac{1}{\bar{r}''} - \frac{1}{\bar{r}'} + \ln \bar{\gamma}'_C(r) - \ln \bar{\gamma}''_C(r) \quad (8)$$

The quantities  $\bar{\gamma}$ , which are the segment molar activity coefficients, may be calculated from the excess Gibbs energy relation.

As discussed earlier [6], Eqs. (5) and (6) directly provide the unknown

distribution functions  $W''(r)$  and  $W'''(r)$ . The other unknowns of the problem ( $Y''$ ,  $\psi''$ ,  $r''$ , and  $\phi$ ) may be calculated from the system of equations obtained by combining equilibrium conditions and material balances:

$$Y''(1 - \psi'') = \frac{Y^F(1 - \psi^F)}{\phi + (1 - \phi) \exp(-r_A \rho_A)} \quad (9)$$

$$(1 - Y'')(1 - \psi'') = \frac{(1 - Y^F)(1 - \psi^F)}{\phi + (1 - \phi) \exp(-r_B \rho_B)} \quad (10)$$

$$\psi'' W'''(r) = \int \frac{K(r)}{\phi} \psi^F W^F(r) dr \quad (11)$$

$$\frac{1}{r''} = \frac{Y''(1 - \psi'')}{r_A} + \frac{(1 - Y'')(1 - \psi'')}{r_B} + \int \frac{K(r)}{r\phi} \psi^F W^F(r) dr \quad (12)$$

with

$$\rho_A = \frac{1}{r''} - \frac{1}{r'} + \ln \bar{\gamma}_A' - \ln \bar{\gamma}_A'' \quad (13)$$

$$\rho_B = \frac{1}{r''} - \frac{1}{r'} + \ln \bar{\gamma}_B' - \ln \bar{\gamma}_B'' \quad (14)$$

### THEORY OF BAKER-WILLIAMS FRACTIONATION

The theory is based on the model described above which subdivides the column fractionation procedure into many local phase equilibria. In this way the phase equilibrium relations presented above can be applied. The considered volume increment  $n$  and the considered column stage  $m$  will be indicated as subscripts of the corresponding quantities, e.g., Eq. (5) now reads

$$\begin{aligned}\psi'_{nm} W'_{nm}(r) &= \frac{1 - K_{nm}(r)}{1 - \phi_{nm}} \psi^F_{nm} W^F_{nm}(r) \\ &= \left\{ \frac{1 - K(r)}{1 - \phi} \psi^F W^F(r) \right\}_{nm}\end{aligned}\quad (15)$$

If an equilibrium  $(nm)$  is established, the sol phase  $(nm)'$  is moved to the next column stage and the gel phase  $(nm)''$  is waiting for the next volume eluent. In contrast to the preceding section, the feed for a LLE does not exist as a homogeneous phase, i.e., the feed  $(n + 1, m + 1)^F$  for the LLE  $(n + 1, m + 1)$  is the union of the mobile sol phase  $(n + 1, m)'$  and the stationary gel phase  $(n, m + 1)''$ . Accordingly multiple, simultaneous phase equilibria are interrelated by the material balances, reading for the polymer

$$\begin{aligned}w'_{n+1,m}(r) + w''_{n,m+1}(r) &= w^F_{n+1,m+1}(r) = w'_{n+1,m+1}(r) + \\ &w''_{n+1,m+1}(r) = \{w'(r) + w''(r)\}_{n+1,m+1}\end{aligned}\quad (16)$$

Here  $w(r)$  is the extensive distribution function, i.e.,  $w(r)dr$  equals the amount of segments of all polymer species with segment numbers between  $r$  and  $r + dr$ . It is interrelated with the intensive distribution function  $W(r)$  according to  $W(r) = w(r)/\bar{n}_C$ , where  $\bar{n}_C$  is the overall amount of segments of all polymer species in the phase considered. Correspondingly, the material balance reads in intensive terms

$$\{\epsilon(1 - \phi)\psi'W'(r)\}_{n+1,m} + \{\epsilon\phi\psi''W''(r)\}_{n,m+1} = \{\epsilon\psi^FW^F(r)\}_{n+1,m+1}\quad (17)$$

$$\{\psi^FW^F(r) = (1 - \phi)\psi'W'(r) + \phi\psi''W''(r)\}_{n+1,m+1}\quad (18)$$

The quantity  $\epsilon_{nm}$  is the ratio of the overall amount of segments (solvent + nonsolvent + polymer) in the feed  $(nm)^F$  and in the feed  $(0,0)^F$ , respectively. It accounts for differences in the overall amounts of segments in the different feeds  $(nm)^F$  and, since these differences are small, it roughly equals unity. At stage  $m = 0$  the condition

$$\epsilon_{n0} = 1\quad (19)$$

is realized by the amount of solvent mixture added. In the other cases  $\epsilon$  follows from the phases combined, leading to

$$\epsilon_{0,m+1} = (1 - \phi_{0m})\epsilon_{0m} = \prod_{i=0}^m (1 - \phi_{0i}); \quad m_P = 0 \tag{20}$$

and

$$\epsilon_{n+1,m+1} = (1 - \phi_{n+1,m})\epsilon_{n+1,m} + \phi_{n,m+1}\epsilon_{n,m+1} \tag{21}$$

The combination of Eqs. (5) and (6), as applied to the equilibrium considered, and of Eq. (17) interrelates the polymer distributions in the feeds of neighboring equilibria

$$\{\epsilon\psi^F W^F(r)\}_{n+1,m+1} = \{\epsilon[1 - K(r)]\psi^F W^F(r)\}_{n+1,m} + \{\epsilon K(r)\psi^F W^F(r)\}_{n,m+1} \tag{22}$$

For the special cases  $m = 0$  and  $n = 0$ , the relation simplifies to

$$\{\epsilon\psi^F W^F(r)\}_{n+1,0} = \{\epsilon K(r)\psi^F W^F(r)\}_{n0} \tag{23}$$

$$\{\epsilon\psi^F W^F(r)\}_{0,m+1} = \{\epsilon[1 - K(r)]\psi^F W^F(r)\}_{0m}; \quad m_P = 0 \tag{24}$$

respectively. Successive substitution according to Eqs. (22)–(24) results in

$$\frac{\{\epsilon\psi^F W^F(r)\}_{nm}}{\psi_{00}^F W_{00}^F(r)} = \sum_{j_m=0}^n \sum_{j_{m-1}=0}^{j_m} \dots \sum_{j_2=0}^{j_3} \sum_{j_1=0}^{j_2}$$

$$\prod_{k=0}^{j_1-1} K_{k0}(r) \prod_{i=1}^m \left[ (1 - K_{j_i, i-1}(r) \prod_{s=j_i}^{j_{i+1}-1} K_{s,i}(r)) \right]$$

with

$$\prod_{i=j}^k ( ) = 1 \text{ if } k < j; \quad m_P = 0 \tag{25}$$

Equation (25) permits the direct and explicit calculation of the various polymer distribution functions  $W_{nm}^F(r)$  from the distribution function  $W_{00}^F(r)$  of the original polymer. The unknowns of Eq. (25) are  $Y_{ij}''$ ,  $\psi_{ij}''$ ,



$r''_{ij}$ , and  $\phi_{ij}$  for  $i = 0, 1, \dots, n$  and  $j = 0, 1, \dots, m$ . These quantities are to be calculated successively. For example, the calculation is first made for  $j = 0$  and  $i = 0, 1, \dots, n$ , and then for  $j = 1$  and  $i = 0, 1, \dots, n$  etc. from Eqs. (9)–(12) as applied to the equilibrium ( $ij$ ). The calculation of the corresponding quantities for the phases ' and for the feeds is possible by applying the material balances as presented in Appendix I. If at the beginning of the fractionation the polymer is precipitated in more than one stage ( $m_p > 0$ ), the relations presented in Appendix II are to be applied.

### COMPUTER SIMULATION

The results presented in the next section are based on the following specifications. The segment molar excess Gibbs energy  $\overline{G}^E$  reads

$$\begin{aligned} \frac{\overline{G}^E}{RT} = & Y(1 - Y)(1 - \psi)^2\chi_{AB} + Y(1 - \psi)\psi\chi_{AC} \\ & + (1 - Y)(1 - \psi)\psi\chi_{BC} \end{aligned} \quad (26)$$

with  $\chi_{AB} = 500K/T$ ,  $\chi_{AC} = 150K/T$ , and  $\chi_{BC} = 250K/T$ .

The distribution of the original polymer is assumed to be described by the Schulz-Flory function

$$W_{00}^F(r) = \frac{r}{150^2} \exp\left(-\frac{r}{150}\right) \quad (27)$$

Furthermore, the following values are applied:  $r_A = 1$ ,  $r_B = 1$ ,  $\psi_{00}^F = 0.02$ ,  $m_p = 2$ ,  $T_0 = 340$  K,  $\Delta T = 2.5$  K,  $Y_{00}^* = 0.01$ ,  $\Delta Y^* = 0.3$ , and  $n^* = 30$ .

In order to simulate a hypothetical column fractionation, special software had to be developed. This was done in FORTRAN 77 for a personal computer in two separate program parts. One part permits the successive calculation of the local equilibria and stores the LLE quantities. The other part is needed to interpret these quantities and to present the results in the desired manner.

The problem is the calculation of hundreds or thousands of connected

equilibria for a system of a solvent, a nonsolvent, and a polydisperse polymer in acceptable time. For each equilibrium ( $nm$ ), the system of Eqs. (9)–(12) has to be solved numerically. Due to the simple structure of Eq. (26), it was possible to eliminate  $r''$  and to reduce, in this way, the system of equations to be solved. In Eqs. (11) and (12) a numerical integration is necessary for the connected equilibria (see Eq. 25). The starting values of the equilibrium calculations are found by approximation routines or, if necessary, by a random procedure. Since the results of each LLE calculation are saved immediately, an interruption and continuation of the column calculation is possible.

## RESULTS

The application of the computer simulation permits the investigation of various effects in the field of column fractionation. In Fig. 1 the calculated polymer distribution functions for two fractions are shown.

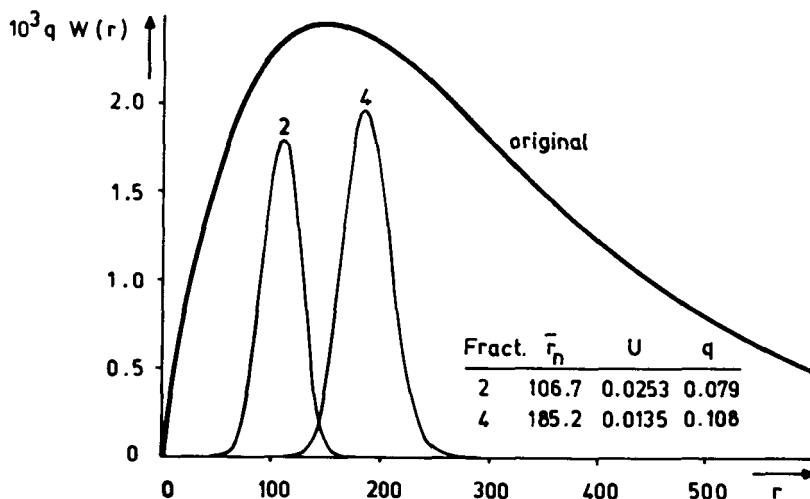


FIG. 1. Polymer distribution functions of Fractions 2 and 4 for a computer-simulated hypothetical Baker-Williams fractionation. Fraction 2 contains the polymer of the volume increments 11 to 20 and Fraction 4 of the volume increments 31 to 40.

The column was subdivided into 13 stages: 3 stages containing the polymer at the start and 10 fractionation stages. The quantity  $q$  is the quotient of the total amount of polymer segments in the phase considered and in the original polymer.  $\bar{r}_n$  and  $\bar{r}_w$  are the number-average and the weight average segment number, respectively, and the nonuniformity  $U$  is defined by  $U = \bar{r}_n/\bar{r}_w - 1$ . The fractionation effect in one of the many equilibria is illustrated in Fig. 2. Due to fractionation, the polymer distribution in the mobile phase ' becomes smaller and smaller while running through the column as shown as Figs. 3 and 4.

An important problem is the relationship between the nonuniformity  $U$  of the fractionated polymer and the number of stages  $m$ . A favorable plot is shown in Fig. 5. If the temperature gradient is properly chosen, the nonuniformity proves, to a rough approximation, to be inversely proportional to the number of stages  $m$ . Deviations occur especially at small values of  $n$ .

Another point of interest is the comparison of fractionation efficiencies for a mixed solvent and a pure solvent. Experimental investigations

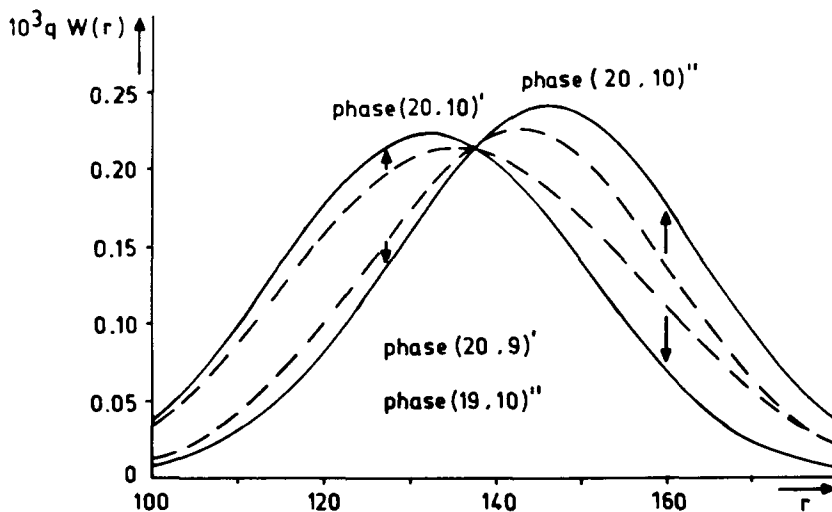


FIG. 2. Liquid-liquid equilibrium ( $n = 20$ ,  $m = 10$ ). (---) Polymer distribution of phases combined. (—) Polymer distribution of the coexisting phases ' and ''.

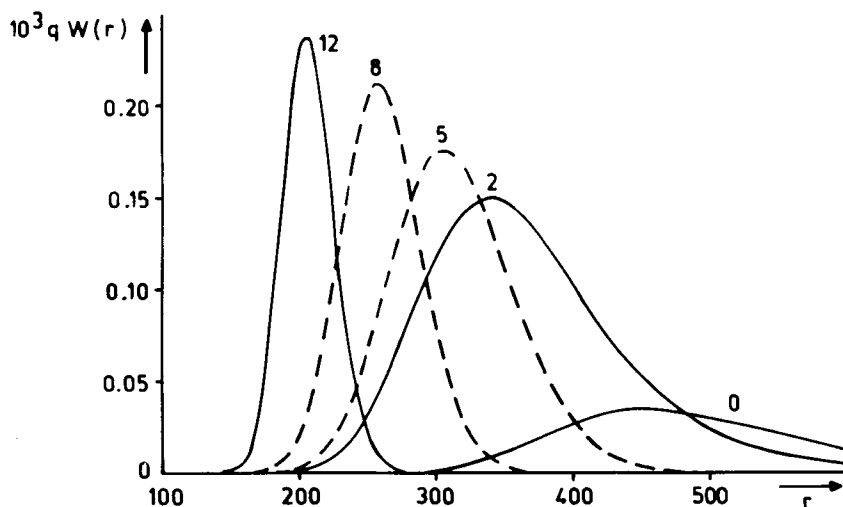


FIG. 3. Polymer distributions in the mobile sol phase ' of volume increment  $n = 40$  at various stages  $m$ .

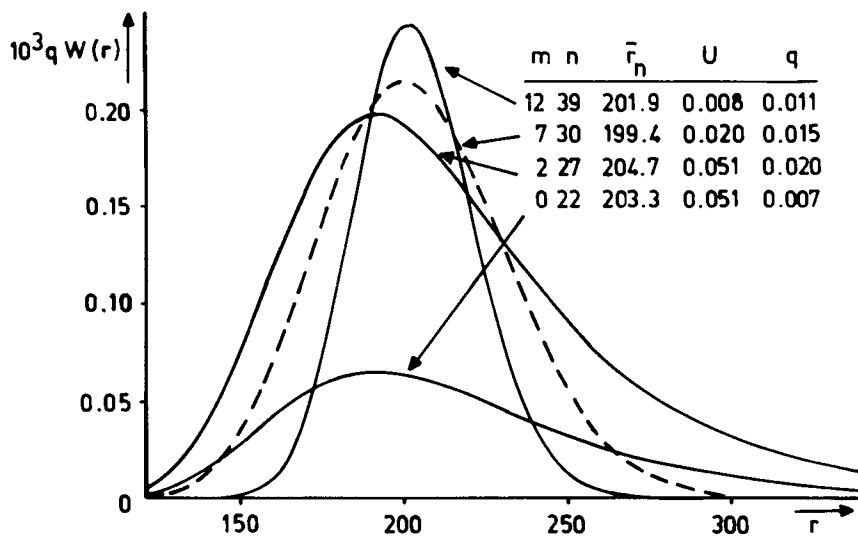


FIG. 4. Fractionation effect in the column, illustrated for some polymer distributions with segment numbers near  $r = 200$  in the mobile phase ' at various stages  $m$ .

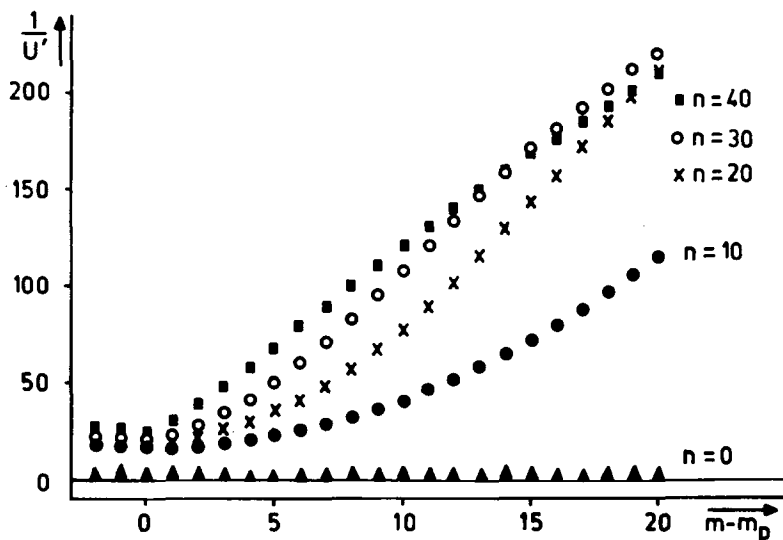


FIG. 5. Favorable plot of the polymer nonuniformity  $U$  in phase ' at different stages  $m$ . In the example shown, the polymer is assumed to be precipitated initially at the first three stages.

on LLE [9, 10] provide nearly the same efficiencies in both cases. Figure 6 shows that the theoretical result conforms to the experimental ones. Calculations with various interaction parameters in Eq. (26) lead to the statements that (i) the fractionation efficiency of a mixed solvent is not better than that of a pure solvent, and (ii) the use of a relatively poor solvent and a relatively inert precipitant (nonsolvent) is favorable for column fractionation.

## APPENDIX I

Calculation of  $\psi'$ ,  $Y'$ , and  $\mathcal{F}'$ :

$$\left\{ \psi' = \frac{\psi^F - \phi \psi''}{1 - \phi} \right\}_{nm} \quad (\text{A.1})$$

$$\left\{ Y' = \frac{Y^F - \phi \frac{1 - \psi''}{1 - \psi^F} Y''}{1 - \phi \frac{1 - \psi''}{1 - \psi^F}} \right\}_{nm} \quad (\text{A.2})$$

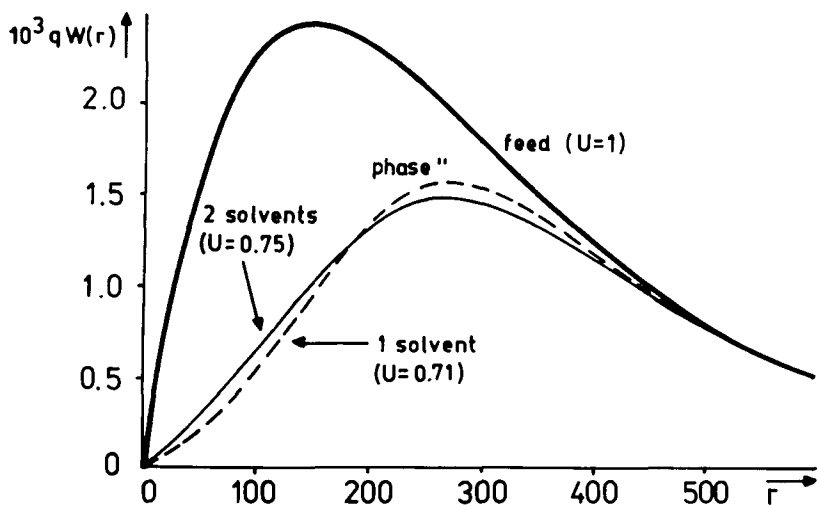


FIG. 6. Comparison of efficiencies for the used mixed solvent and a pure solvent. Conditions: For  $n = 0$ ,  $m = 0$ :  $\Psi = 0.02$ ,  $q'' = 0.659$ . Mixed solvent:  $Y_{00}^* = 0.22$ ,  $T_0 = 340$  K. Pure solvent:  $Y = 0$ ,  $\chi_{BC} = 0.6015$ .

$$\left\{ \frac{1}{r'} = \frac{\frac{1}{r^F} - \phi \frac{1}{r''}}{1 - \phi} \right\}_{nm} \quad (\text{A.3})$$

Calculation of  $\psi^F$ :

$$\{\epsilon\psi^F\}_{n+1,m+1} = \{\epsilon(1 - \phi)\psi'\}_{n+1,m} + \{\epsilon\phi\psi''\}_{n,m+1} \quad (\text{A.4})$$

For  $n = 0$ , Eq. (A.4) simplifies to

$$\psi_{0,m+1}^F = \psi'_{0m}; \quad m_p = 0 \quad (\text{A.5})$$

and for  $m = 0$  to

$$\psi_{n+1,0}^F = \{\phi\psi''\}_{n0} \quad (\text{A.6})$$

Calculation of  $Y^F$ :

$$\{\epsilon Y^F(1 - \psi^F)\}_{n+1, m+1} = \{\epsilon(1 - \phi)Y'(1 - \psi')\}_{n+1, m} + \{\epsilon\phi Y''(1 - \psi'')\}_{n, m+1} \quad (\text{A.7})$$

$$Y_{0, m+1}^F = Y_{0m}'; \quad n = 0 \quad (\text{A.8})$$

$$\{Y^F(1 - \psi^F)\}_{n+1, 0} = \{\phi Y''(1 - \psi'')\}_{n0} + (1 - \phi_{n0})Y_{n+1, 0}^*; \quad m = 0 \quad (\text{A.9})$$

where  $Y^*$  is given by Eq. (2).

Calculation of  $\mathcal{F}_C^F$ :

$$\left\{ \frac{\epsilon \psi^F}{\mathcal{F}_C^F} \right\}_{n+1, m+1} = \left\{ \frac{\epsilon(1 - \phi)\psi'}{\mathcal{F}'_C} \right\}_{n+1, m} + \left\{ \frac{\epsilon\phi\psi''}{\mathcal{F}''_C} \right\}_{n, m+1} \quad (\text{A.10})$$

$$\mathcal{F}_{C, 0, m+1}^F = \mathcal{F}'_{C, 0m}; \quad m_p = 0, n = 0 \quad (\text{A.11})$$

$$\mathcal{F}_{C, n+1, 0}^F = \mathcal{F}''_{C, n0}; \quad m = 0 \quad (\text{A.12})$$

## APPENDIX II

Modification of Eqs. (20), (24), (A.5), and (A.11) for the case  $m_p > 0$ :

$$\epsilon_{0, m+1} = (1 - \phi_{0m})\epsilon_{0m} + \delta\psi_{00}^F$$

$$\delta = 1 \text{ if } m + 1 \leq m_p; \delta = 0 \text{ if } m + 1 > m_p \quad (\text{A.13})$$

$$\{\epsilon\psi^F W^F(r)\}_{0, m+1} = \{\epsilon[1 - K(r)]\psi^F W^F(r)\}_{0m} + \delta\{\psi^F W^F(r)\}_{00} \quad (\text{A.14})$$

$$\{\epsilon\psi^F\}_{0, m+1} = \{\epsilon(1 - \phi)\psi'\}_{0m} + \delta\psi_{00}^F \quad (\text{A.15})$$

$$\left\{ \frac{\epsilon\psi^F}{\mathcal{F}_C^F} \right\}_{0, m+1} = \left\{ \frac{\epsilon(1 - \phi)\psi'}{\mathcal{F}'_C} \right\}_{0m} + \delta \frac{\psi_{00}^F}{\mathcal{F}_{C, 00}^F} \quad (\text{A.16})$$

## REFERENCES

- [1] C. A. Baker and R. J. P. Williams, *J. Chem. Soc.*, p. 2352 (1956).
- [2] S. R. Caplan, *J. Polym. Sci.*, **35**, 409 (1959).
- [3] G. V. Schulz, P. Deussen, and A. G. R. Scholz, *Makromol. Chem.*, **69**, 47 (1963).

- [4] G. V. Schulz, K. C. Berger, and A. G. R. Scholz, *Ber. Bunsenges. Phys. Chem.*, **69**, 856 (1965).
- [5] W. V. Smith, *J. Polym. Sci., Part A-2*, **8**, 207 (1970).
- [6] M. T. Rätzsch, H. Kehlen, and L. Tschersich, *J. Macromol. Sci. – Chem.*, **A26**, 921 (1989).
- [7] H. Kehlen and M. T. Rätzsch, *Z. Phys. Chem. (Leipzig)*, **264**, 1153 (1983).
- [8] M. T. Rätzsch and H. Kehlen, *J. Macromol. Sci. – Chem.*, **A22**, 323 (1985).
- [9] J. W. Breitenbach and B. A. Wolf, *Makromol. Chem.*, **108**, 263 (1967).
- [10] H. J. Mencer and B. Kunst, *Ibid.*, **180**, 2463 (1979).

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