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APPLICATION OF CONTINUOUS THERMODYNAMICS TO POLYMER FRACTIONATION

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ABSTRACT

Continuous thermodynamics was developed in recent years and applied successfully to the liquid-liquid equilibrium of polydisperse polymer solutions. Continuous thermodynamics is based on the direct use of continuous distribution functions in the thermodynamic equations. There is no need for a reduction to pseudocomponents. This paper presents the application of continuous thermodynamics to successive polymer fractionation procedures based on solubility differences. In this way, simple equations for the distribution function of the different polymer fractions are obtained. Furthermore, the other equations describing the fractionation possess a lucid structure favorable for computer simulations of the fractionation procedures.

INTRODUCTION

Fractionation is the most important method to investigate the composition of polydisperse polymers. Small differences in solubility of the polymer species with different molecular weights are used for separating the polymer species. G. B. Schulz [1, 2] was the first to present a mathematical treatment of successive fractionation experiments. In the 1960s and 1970s Tung [3], Koningsveld and Stavermann [4], as well as Kamide et al. [5-8], simulated a number of successive fractionation processes. In all these papers, pseudocomponents were used to describe the polymer polydispersity.

Continuous thermodynamics has been developed within the last four years and has proved to be the most convenient method for treating the polydispersity of many industrially important mixtures. This method was applied to vapor-liquid equilibrium, especially of complex hydrocarbon systems, to liquid-liquid equilibrium, especially of polymer solutions and of polymer mixtures, and to stability considerations. In continuous thermodynamics the distribution functions describing the polydispersity are directly used in the thermodynamic calculations without an arbitrary splitting into pseudocomponents. In this paper, continuous thermodynamics is applied to three different fractionation procedures for polydisperse polymers: successive precipitation, successive dissolution, and refractionation.

PHASE EQUILIBRIUM

The liquid-liquid equilibrium (LLE) of polymer solutions forms the thermodynamic background for these fractionation procedures. The treatment of the LLE by continuous thermodynamics was presented earlier [9, 10]. Only the most important equations will be summarized here, and a somewhat different formulation convenient for generalization to fractionations will be introduced.

A solution of a Solvent A and a polydisperse Polymer B is considered. The individual species of Polymer B are identified by their segment numbers, r, which is defined as the ratio of the hard-core volume of the species considered to the hard-core volume of an arbitrarily chosen standard segment. This results in

$$r = M/M_{\text{seg}}, \tag{1}$$

where M is the molecular weight of the polymer species considered and M_{seg} is the molecular weight of a polymer segment possessing the same hard-core volume as the chosen standard segment.

The essence of continuous thermodynamics consists in considering M and r as continuously variable quantities. The segment number of the solvent is r_A. The composition of the polymer is described by the distribution function $W(r)$, defined by the statement that $W(r)dr$ gives the fraction of all polymer segments that come from those polymeric species with segment numbers between r and $r + dr$. If r_0 is the lowest and r^0 the highest occurring segment number of polymer molecules, the normalization relation reads

$$\int W(r)dr = 1; \quad \text{where} \int \text{represents} \int_{r_0}^{r^0}. \tag{2}$$

In continuous thermodynamics the condition for equilibrium between two Phases $'$ and $''$ as expressed by the chemical potentials is written

$$\mu_A{}' = \mu_A{}'', \tag{3}$$

$$\mu_B{}'(r) = \mu_B{}''(r). \tag{4}$$

Equation (4) is valid for all segment numbers occurring from r_0 to r^0.

The chemical potentials may be written as follows [9, 10] by considering the pressure to be constant:

$$\mu_A = \mu_A{}^*(T) + RT\left[\ln(1-\psi) + 1 - \frac{r_A}{\bar{r}}\right] + r_A RT \ln \bar{\bar{\gamma}}_A, \tag{5}$$

$$\mu_B(r) = \mu_{B,0}{}^*(r,T) + RT\left[\ln \psi W(r) + 1 - \frac{r}{\bar{r}}\right] + rRT \ln \bar{\bar{\gamma}}_B(r). \tag{6}$$

The first term is the reference chemical potential, the second term is the well-known Flory-Huggins contribution (with $\chi = 0$), and the last term describes the deviation from such a Flory-Huggins mixture. The quantities $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B(r)$, named segment molar activity coefficients, are introduced for this purpose, and in the general case they depend on T, ψ, and $W(r)$. ψ is the overall segment fraction of the polymer, and $\bar{r}$ is the number-average segment number for the phase considered, defined by

$$\frac{1}{\bar{r}} = \frac{1-\psi}{r_A} + \frac{\psi}{\bar{r}_B}; \quad \frac{1}{\bar{r}_B} = \int \frac{W(r)}{r} dr. \tag{7}$$

Combination of Eqs. (3) and (4) with Eqs. (5) and (6) results in

$$1 - \psi'' = (1 - \psi') \exp(r_A \rho_A), \tag{8}$$

$$\psi'' W''(r) = \psi' W'(r) \exp(r \rho_B(r)), \tag{9}$$

with

$$\rho_A = \frac{1}{\bar{r}''} - \frac{1}{\bar{r}'} + \ln \bar{\bar{\gamma}}_A{}' - \ln \bar{\bar{\gamma}}_A{}'', \tag{10}$$

$$\rho_B(r) = \frac{1}{\bar{r}''} - \frac{1}{\bar{r}'} + \ln \bar{\bar{\gamma}}_B{}'(r) - \ln \bar{\bar{\gamma}}_B{}''(r). \tag{11}$$

In phase-separation experiments, a feed phase F is split into the two coexisting Phases $'$ and $''$. The fraction of the feed volume that forms Phase $''$ is given by the quantity ϕ, i.e., ϕ equals the total amount of segments (polymer and solvent in Phase $''$ divided by the total amount of segments (polymer and solvent) in the feed. Hence, the mass balance for the polymer species in continuous thermodynamics reads

$$\psi^F W^F(r) = (1 - \phi)\psi' W'(r) + \phi \psi'' W''(r), \tag{12}$$

and, after integration,

$$\psi^F = (1 - \phi)\psi' + \phi \psi''. \tag{13}$$

Equation (7) with Eqs. (12) and (13) leads to the relation

$$\frac{1}{\bar{r}^F} = \frac{1 - \phi}{\bar{r}'} + \frac{\phi}{\bar{r}''}. \tag{14}$$

In phase-separation experiments the composition of the feed (i.e., ψ^F and $W^F(r)$) is usually known. The relations between the quantities referring to Phase $'$ and those referring to Phase $''$ are provided by Eqs. (12)-(14), which permit the elimination of the quantities of one of the two coexisting phases, e.g., of those referring to Phase $'$.

Combination of Eqs. (9) and (12) results in

$$\psi'' W''(r) = \frac{\psi^F W^F(r)}{\phi + (1 - \phi)\exp\left[-r\rho_B(r)\right]}. \tag{15}$$

This equation interrelates the distribution function $W''(r)$ in the unknown Phase $''$ and the feed distribution $W^F(r)$.

In applying this relation, one has to keep in mind that, in the general case, $\rho_B(r)$ also depends on $W''(r)$ via $\bar{\bar{\gamma}}_B{}'(r)$ and $\bar{\bar{\gamma}}_B{}''(r)$ according to Eq. (11).

The expressions for the segment-molar activity coefficients, $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B(r)$, are obtained from the excess Gibbs energy relation used [9, 10]. In the general case, the excess Gibbs energy depends on T, ψ, and the distribution function $W(r)$. But in many relations used in practice, the dependence on $W(r)$ is neglected as an acceptable approximation. Then the segment-molar activity coefficients also do not depend on $W(r)$, and $\bar{\bar{\gamma}}_B$ does not depend on the independent variable r [9, 10]. Then ρ_B also does not depend on r, and it depends on $W''(r)$ only by way of $\bar{r}''$. This quantity is a function of $W''(r)$, i.e., a number. Considering this number as an additional unknown of the problem, Eq. (15) provides a direct and explicit relation for calculation of $W''(r)$ from the feed distribution $W^F(r)$.

Of course, this relation contains the unknowns of the problem, ψ'', $\bar{r}''$, and ϕ (or T), but these quantities are simply unknown *numbers* and not unknown *functions*. Hence, it proves possible in this way to separate the problem of the unknown distribution functions from the problem of the other unknowns and to solve the function problem exactly. A simple example for this possibility is provided by Huggins' χ-parameter concept

$$r_A \ln \bar{\bar{\gamma}}_A = \chi\psi^2; \qquad r_A \ln \bar{\bar{\gamma}}_B = \chi(1-\psi)^2; \qquad \chi = \chi(T). \tag{16}$$

If, on the other hand, the excess Gibbs energy depends on the distribution function, then this dependence usually is provided by the occurrence of further functionals (e.g., moments) of the distribution function. This means that, in this case also, the separation is possible and that the exact solution of the distribution function problem is again provided by Eq. (15). The only difference is that, in addition to ψ'', $\bar{r}''$, and ϕ (or T), the functionals mentioned occur as further unknown numbers of the problem. In the following, for simplicity, such additional unknowns are assumed not to occur. However, the generalization to more general cases is straightforward.

In treating polymer fractionation, it is convenient to introduce the precipitation rate K [1, 11, 12]. In the continuous case, K is a continuous function of r defined as the quotient of the amounts of segments of all polymer species with segment numbers between r and $r + dr$ in phase $''$ and in the feed phase F, respectively:

$$K(r) = \phi \frac{\psi'' W''(r)dr}{\psi^F W^F(r)dr} = \phi \frac{\psi'' W''(r)}{\psi^F W^F(r)}. \tag{17}$$

Equation (15) permits us to write

$$K(r) = \frac{\phi}{\phi + (1 - \phi) \exp\,[-r\rho_B(r)]}. \tag{18}$$

The introduction of the precipitation rate $K(r)$ permits us to obtain from Eqs. (12) and (15) the simple relations

$$\psi' W'(r) = \frac{1 - K(r)}{1 - \phi} \psi^F W^F(r), \tag{19}$$

$$\psi'' W''(r) = \frac{K(r)}{\phi} \psi^F W^F(r). \tag{20}$$

As discussed above, these relations provide the unknown distribution functions $W'(r)$ and $W''(r)$ directly. The other unknowns of the problem, ψ'', $\bar{r}''$, and ϕ (or T), may be calculated from the relations

$$1 - \psi'' = \frac{1 - \psi^F}{\phi + (1 - \phi) \exp\,(-r_A \rho_A)}, \tag{21}$$

$$\psi'' = \int \frac{K(r)}{\phi} \psi^F W^F(r) dr, \tag{22}$$

$$\frac{1}{\bar{r}''} = \frac{1 - \psi''}{r_A} + \int \frac{1}{r} \frac{K(r)}{\phi} \psi^F W^F(r) dr. \tag{23}$$

Equations (21)-(23) are obtained from Eqs. (8) and (13), from Eqs. (2) and (20), and from the Eqs. (7) and (22), respectively.

FRACTIONATION PROCEDURES

Figure 1 presents the schemes for successive precipitation fractionation (SPF) [7], successive solution fractionation (SSF) [7], and a refractionation (RF) [5]. In all three cases a homogeneous polymer solution, called "feed phase F," by lowering the temperature is split into two coexisting phases, a polymer-lean Phase $'$ and a polymer-rich Phase $''$, which are then separated. In SPF the polymer is isolated from Phase $''$ as Fraction 1. Phase $'$ directly forms the feed phase for the next fractionation step, etc.

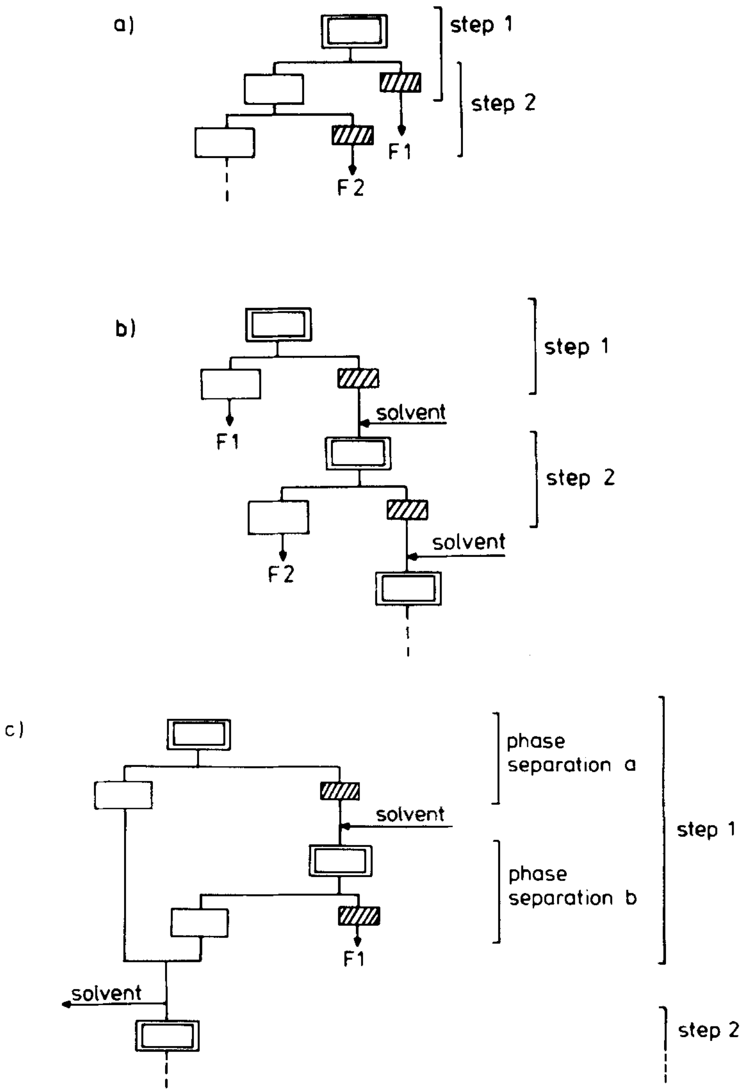

FIG. 1. Schemes of fractionation procedures. a) Successive precipitation fractionation (SPF), b) successive solution fractionation (SSF), and c) refractionation (RF). Double rectangles: Original feed phase or intermediate feed phases with amounts of segments equal to that in the original feed phase. Single rectangles: Phase $'$ (polymer-lean phase). Striped rectangles: Phase $''$ (polymer-rich phase), $F1$, $F2$, . . . = Fraction 1, Fraction 2, ...

In the case of SSF, Fraction 1 is obtained from Phase $'$. Phase $''$ is diluted by adding solvent up to the volume of the original feed phase, corresponding, to a very good approximation, to the same total amount of segments. This phase is used as the feed phase for Step 2, etc.

In the RF procedure, each step consists of two phase separations. The separation described above is signified by phase separation *a*. The Phase $''$ obtained in this separation is diluted up to the volume of the original feed in the same way as in the SSF procedure, and then it forms the feed for phase separation *b*. Fraction 1 is isolated from the polymer-rich Phase $''$ of this phase separation *b*. The polymer-lean Phases $'$ of the separations *a* and *b* are united and concentrated up to the volume of the original feed phase. This phase now forms the feed for Step 2, etc.

In the last fractionation step the polymer of Phase $'$ in the case of SPF, of Phase $''$ in the case of SSF, and of the united Phases $'$ for RF forms the final polymer fraction.

All coexisting pairs of Phases $'$ and $''$ are presumed to be in equilibrium. Hence, it is possible to apply Eqs. (1)-(23). To indicate the different separation steps 1, 2, . . ., the corresponding number, in general *i*, *j*, or *k*, is added as a subscript.

In the case of refractionation it is necessary to distinguish between the two phase separations *a* and *b* in each fractionation step. This is done by adding the letters *a* or *b* to the subscript, respectively.

SUCCESSIVE PRECIPITATION FRACTIONATION

In SPF, Phase $'$ from Step *i* is used directly as the feed phase for Step (*i* + 1). Hence, the following relations are valid:

$$\psi_{i+1}^{F} = \psi_i', \tag{24}$$

$$W_{i+1}^{F}(r) = W_i'(r), \tag{25}$$

$$\bar{r}_{i+1}^{F} = \bar{r}_i'. \tag{26}$$

On adding the Subscript *i*, Eq. (20) reads

$$\psi_i'' W_i''(r) = \frac{K_i(r)}{\phi_i} \psi_i^F W_i^F(r). \tag{27}$$

Use of Eqs. (19), (24), and (25) for successive substitutions results in

$$\psi_i''W_i''(r) = \frac{K_i(r)}{\phi_i} \prod_{j=1}^{i-1} \frac{1 - K_j(r)}{1 - \phi_j} \psi_1^F W_1^F(r). \tag{28}$$

Equation (28) permits the direct and explicit calculation of the distribution function of the polymer fraction i, $W_i''(r)$, from the distribution function $W_1^F(r)$ of the original polymer. The form of this relation corresponds to the fractionation scheme applied. In Steps $j = 1, \ldots, i - 1$ the polymer-lean Phase $'$ is taken to correspond to the occurrence of the factor $(1 - K_j(r))/(1 - \phi_j)$ for $j = 1, \ldots, i - 1$, according to Eq. (19). In Step i, the polymer-rich Phase $''$ is taken to correspond to the factor $K_i(r)/\phi_i$, according to Eq. (20).

To perform the calculation, the composition of the original polymer solution, i.e., ψ_1^F and $W_1^F(r)$, must be given. Furthermore, Eq. (28) contains the unknowns ψ_j'', $\bar{r}_j''$, and ϕ_j (or T_j) for $j = 1, \ldots, i$. These quantities are to be calculated successively, i.e., at first for $j = 1$, then for $j = 2$, etc., from the relations

$$1 - \psi_j'' = \frac{1 - \psi_j^F}{\phi_j + (1 - \phi_j)\exp(-r_A \rho_{Aj})}, \tag{29}$$

$$\psi_j'' = \int \frac{K_j(r)}{\phi_j} \prod_{k=1}^{j-1} \frac{1 - K_k(r)}{1 - \phi_k} \psi_1^F W_1^F(r) dr, \tag{30}$$

$$\frac{1}{\bar{r}_j''} = \frac{1 - \psi_j''}{r_A} + \int \frac{1}{r} \frac{K_j(r)}{\phi_j} \prod_{k=1}^{j-1} \frac{1 - K_k(r)}{1 - \phi_k} \psi_1^F W_1^F(r) dr. \tag{31}$$

Equation (29) is Eq. (21) as applied to Step j. Equation (30) is obtained in an analogous way from Eq. (28) by integration, and Eq. (31) is obtained analogously from Eq. (7) and Eq. (28).

SUCCESSIVE SOLUTION FRACTIONATION

According to the remarks made above, the total number of segments in SSF is the same to a very good approximation in all feed phases. This leads to the relation

$$\psi_{i+1}^F W_{i+1}^F(r) = \phi_i \psi_i'' W_i''(r). \tag{32}$$

From Eqs. (19) and (20), as applied to fractionation Step *i*, the distribution function of the *i*th polymer fraction $W_i'(r)$ can be derived in a direct and explicit form:

$$\psi_i' W_i'(r) = \frac{1 - K_i(r)}{1 - \phi_i} \prod_{j=1}^{i-1} K_j(r) \psi_1{}^F W_1{}^F(r). \tag{33}$$

Again, this relation corresponds to the fractionation scheme. In Steps $j = 1, \ldots, i - 1$, the polymer-rich Phase $''$ is taken to correspond to the occurrence of the factor $K_j(r)$ for $j = 1, \ldots, i - 1$, according to Eq. (20). (The denominator ϕ is absent due to the occurrence of ϕ in Eq. 32.) The polymer-lean Phase $'$ in Step *i* is taken to correspond to the factor $(1 - K_i(r))/(1 - \phi_i)$, according to Eq. (19). The unknown quantities ψ_j'', $\bar{r}_j''$, and ϕ_j (or T_j) for $j = 1, \ldots, i$ can be calculated successively with the help of the three equations

$$1 - \psi_j'' = \frac{1 - \psi_i{}^F}{\phi_j + (1 - \phi_j) \exp(-r_A \rho_{Aj})}, \tag{34}$$

$$\psi_j'' = \int \frac{K_j(r)}{\phi_j} \prod_{k=1}^{j-1} K_k(r) \psi_1{}^F W_1{}^F(r) dr, \tag{35}$$

$$\frac{1}{\bar{r}_j''} = \frac{1 - \psi_j''}{r_A} + \int \frac{1}{r} \frac{K_j(r)}{\phi_j} \prod_{k=1}^{j-1} K_k(r) \psi_1{}^F W_1{}^F(r) dr. \tag{36}$$

These relations correspond to Eqs. (29)-(31) for the case of SPF.

REFRACTIONATION

The continuous thermodynamic treatment of both basic types of successive fractionation, SPF and SSF, has been shown above. Other successive fractionation procedures can be treated by an appropriate combination of these two types.

In the refractionation discussed above (Fig. 1c), the following relations are valid:

$$\psi_{ib}{}^F W_{ib}{}^F(r) = \phi_{ia}''\psi_{ia}''W_{ia}''(r), \tag{37}$$

$$\psi^F_{(i+1)a}W^F_{(i+1)a}(r) = \psi_{ia}{}^F W_{ia}{}^F(r) - \phi_{ib}\psi_{ib}''W_{ib}''(r). \tag{38}$$

From Eq. (27), after adding the index *a* or *b*, these relations become

$$\psi^F_{(i+1)a}W^F_{(i+1)a}(r) = [1 - K_{ia}(r)K_{ib}(r)]\,\psi_{ia}{}^F W_{ia}{}^F(r), \tag{39}$$

and, by successive substitution, give

$$\psi_{ia}''W_{ia}''(r) = \frac{K_{ia}(r)}{\phi_{ia}} \prod_{j=1}^{i-1} [1 - K_{ja}(r)K_{jb}(r)]\,\psi_{1a}{}^F W_{1a}{}^F(r), \tag{40}$$

$$\psi_{ib}''W_{ib}''(r) = \frac{K_{ia}(r)K_{ib}(r)}{\phi_{ib}} \prod_{j=1}^{i-1} [1 - K_{ja}(r)K_{jb}(r)]\,\psi_{1a}{}^F W_{1a}{}^F(r). \tag{41}$$

Here, $W_{ib}''(r)$ is the distribution function of Fraction *i*. Equation (41) permits the direct and explicit calculation of $W_{ib}''(r)$ from the distribution function $W_{1a}{}^F(r)$ of the original polymer. The structure of this relation corresponds to the fractionation scheme (Fig. 1c). The factor $[1 - K_{ia}(r)K_{ib}(r)]$ occurs in the Steps $j = 1, \ldots, i - 1$ according to Eq. (39). In Step *i*, Phase $''$ is taken for phase separation *a* as well as *b*, resulting in the occurrence of the factors K_{ia}/ϕ_{ia} and K_{ib}/ϕ_{ib} according to Eq. (27). Finally, ϕ_{ia} cancels according to the balance of Eq. (37).

To perform the calculation, the composition of the original polymer solution, i.e., $\psi_{1a}{}^F$ and $W_{1a}{}^F(r)$, must be given. Furthermore, Eq. (41) contains the unknowns ψ_{ja}'', ψ_{jb}'', $\bar{r}_{ja}''$, $\bar{r}_{jb}''$, ϕ_{ja}, and ϕ_{jb} (or T_{ja} and T_{jb}) for $j = 1, \ldots, i$. These quantities are to be calculated step by step in the series $j = 1$, $j = 2$, etc. The quantities referring to phase separation *a* can be computed from the relations

$$1 - \psi_{ja}'' = \frac{1 - \psi_{ja}{}^F}{\phi_{ja} + (1 - \phi_{ja})\exp(-r_{\mathrm{A}}\rho_{\mathrm{A},ja})}, \tag{42}$$

$$\psi_{ja}'' = \frac{K_{ja}(r)}{\phi_{ja}} \prod_{k=1}^{j-1} [1 - K_{ka}(r)K_{kb}(r)]\,\psi_{1a}{}^F W_{1a}{}^F(r)dr, \tag{43}$$

$$\frac{1}{\bar{r}_{ja}''} = \frac{1 - \psi_{ja}''}{r_{\mathrm{A}}} + \int \frac{1}{r} \frac{K_{ja}(r)}{\phi_{ja}} \prod_{k=1}^{j-1} [1 - K_{ka}(r) K_{kb}(r)] \, \psi_{1a}{}^{F} W_{1a}{}^{F}(r) dr. \tag{44}$$

These relations correspond to Eqs. (29)-(31) for SPF. They differ in the use of Eq. (40) for refractionation instead of Eq. (28) for SPF. When the quantities ψ_{ja}'', $\bar{r}_{ja}''$, and ϕ_{ja} (or T_{ja}) are known in this way, the unknowns ψ_{jb}'', $\bar{r}_{jb}''$, and ϕ_{jb} (or T_{jb}) may be computed from the relations

$$1 - \psi_{jb}'' = \frac{1 - \psi_{jb}{}^{F}}{\phi_{jb} + (1 - \phi_{jb}) \exp(-r_{\mathrm{A}} \rho_{\mathrm{A}\,jb})}, \tag{45}$$

$$\psi_{jb}'' = \int \frac{K_{ja}(r) K_{jb}(r)}{\phi_{jb}} \prod_{k=1}^{j-1} [1 - K_{ka}(r) K_{kb}(r)] \, \psi_{1a}{}^{F} W_{1a}{}^{F}(r) dr, \tag{46}$$

$$\frac{1}{\bar{r}_{jb}''} = \frac{1 - \psi_{jb}''}{r_{\mathrm{A}}} + \int \frac{K_{ja}(r) K_{jb}(r)}{\phi_{jb}} \prod_{k=1}^{j=1} [1 - K_{ka}(r) K_{kb}(r)] \, \psi_{1a}{}^{F} W_{1a}{}^{F}(r) dr. \tag{47}$$

These relations for phase separation b completely correspond to Eqs. (42)-(44) for phase separation a.

EXAMPLE

A computer-simulated refractionation according to Fig. 1(c) will be considered as an example. To perform the calculations, specific conditions must be chosen. The composition of the original polymer solution shall be given by

$$\psi_{1a}{}^{F} = 0.01, \tag{48}$$

where the polymer distribution is assumed to be described by the Schulz-Flory function

$$W_{1a}{}^{F}(r) = \frac{r}{150^2} \exp\left(-\frac{r}{150}\right). \tag{49}$$

The segment-molar activity coefficients shall be given by the Huggins χ-parameter concept, Eq. (16), adding the subscripts *ia* or *ib*. Furthermore, two of the four quantities ϕ_{ia}, T_{ia}, ϕ_{ib}, and T_{ib} are to be chosen arbitrarily. This is done 1) by choosing $T_{ia} = T_{ib}$, resulting in

$$\chi_{ia} = \chi_{ib}, \tag{50}$$

according to Eq. (16), and 2) by stating that there shall be five fractions containing equal masses, i.e., equal amounts of segments of the polymer. On introducing the quantities q_{ia} and q_{ib} as the quotients of the total amount of polymer segments in Phase '' of the considered phase separation and in the original polymer, respectively, i.e.,

$$q_{ia} = \frac{\phi_{ia}\psi_{ia}''}{\psi_{ia}^F}, \quad q_{ib} = \frac{\phi_{ib}\psi_{ib}''}{\psi_{ia}^F}, \tag{51}$$

Condition 2) may be expressed by

$$q_{ib} = 0.2, \quad i = 1, \ldots, 4. \tag{52}$$

The system of Eqs. (42)-(47) was solved numerically for these conditions. Due to the simple structure of Eqs. (42) and (45), it was possible to eliminate $\bar{r}_{ia}''$ and $\bar{r}_{ib}''$ and to reduce, in this way, the system of equations to be solved.

The results of the computer simulation are presented in Table 1 and in Fig. 2. The number-average segment number $\bar{r}_n$ and the weight-average segment number $\bar{r}_w$ are obtained from

$$\frac{1}{\bar{r}_n} = \int \frac{1}{r} W_{ib}''(r)dr, \tag{53}$$

TABLE 1. Computer Simulation of Refractionation

Fraction	$\bar{r}_n$	$\bar{r}_w$	$(\bar{r}_w/\bar{r}_n) - 1$	q_{ia}	χ_{ia}	ψ_{ia}''	ψ_{ib}''
Original	150	300	1.0	–	–	–	–
1	524.6	597.6	0.14	0.354	0.584	0.181	0.190
2	351.0	381.3	0.09	0.332	0.606	0.224	0.231
3	247.4	265.3	0.07	0.293	0.635	0.279	0.285
4	162.1	174.2	0.07	0.248	0.692	0.371	0.374
5	54.4	81.5	0.50	–	–	–	–

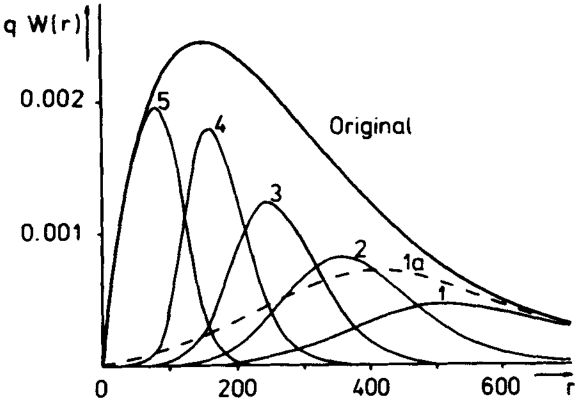

FIG. 2. Computer simulation of refractionation. Distribution functions multiplied by q for the original polymer ($q = 1$) and for Fractions 1-5. Curve 1a refers to phase separation a in Step 1.

$$\bar{r}_w = \int r W_{ib}''(r) dr, \tag{54}$$

and $(\bar{r}_w/\bar{r}_n) - 1$ measures the degree of heterogeneity.

Figure 2 presents the distribution functions of polymer fractions 1-5 multiplied by the corresponding value of q. Therefore, summation of Curves 1-5 results in the curve for the original polymer. In the example, q equals 0.2 for all five fractions. Curve 1a shows the distribution function $W_{1a}''(r)$ multiplied by q_{1a}.

Comparison of the example presented in Table 1 and Fig. 2 with other examples based on other conditions shows that equality of temperatures for phase separations a and b in each step is a very favorable experimental condition. The fractionation efficiency is near the optimum.

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