Phase-Equilibrium Fractionation of Continuous Distributions

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Fractionation of continuously distributed homologous mixtures is described in terms of molecular distributions. The concepts apply to phase equilibrium in vapor−liquid hydrocarbon mixtures and sol−gel polymer mixtures. Models of both differential and finite phase-equilibrium separations are presented when the partition coefficient for the equilibrium distributions is given. Analytical solutions for the distributions, including a similarity solution for a differential fractionation, can be formed. A differential fractionation solution compares satisfactorily with experimental data.

Introduction

Increased attention has recently been directed to phase-equilibrium fractionation for systems that have a continuously distributed variable, for example, molecular weight (MW) (Evans et al., 1998; Fredrickson, 1998; Ratzsch et al., 1991). The subject has a history that includes polymer fractionations by precipitation and solubilization methods (Francuskiewicz, 1994; Cooper, 1989), and hydrocarbon separations by vaporization or condensation (Sandler and Libby, 1991; Kehlen and Ratzsch, 1987; Cotterman and Prausnitz, 1985). Separations may occur for arbitrary amounts of each phase in equilibrium (flash fractionation), or for an infinitesimal amount of one equilibrium phase (cloud point). After equilibrium is established, the separate phases can be isolated and treated again. For vapor−liquid equilibrium, dew and bubble points are cloud points with infinitesimal amounts of liquid or of vapor, respectively. If the infinitesimal fraction is removed and recovered for each subsequent cloud point, the process is a differential fractionation, such as batch distillation (Treybal, 1980). Analytical solutions for multicomponent mixtures, usually difficult or impossible for discrete systems, are often straightforward for continuously distributed systems.

Kamide and Matsuda (1989) reviewed polymer fractionation methods, in particular, successive precipitation fractionation and successive solution fractionation, with the main objective to determine the molecular-weight distributions (MWDs). The methods involve polymer partitioning either by precipitation or solvent dissolution and then analyzing each phase for polymer amount. Solvent is added or removed in a sequence of steps, as in a cascade of equilibrium stages. Sequential partitioning yields separated polymer fractions. Semiempirical theories to describe phase-equilibrium fractionations were based on approximate thermodynamic relationships employing fitting parameters (Kamide, 1977).

Chemical engineers have explored continuous-mixture thermodynamic models of vapor−liquid hydrocarbon separations for their important industrial applications. Using an equation-of-state for alkanes, Cotterman et al. (1985) provided Raoult's law calculations for vapor−liquid equilibrium, including bubble- and dew-points, of *n*-paraffins. The method was also applied to flash liquid−liquid (or sol−gel) fractionation of polydisperse polymer in solution. Continuous thermodynamics was applied to multicomponent column distillation (Kehlen and Ratzsch, 1987), to vapor−liquid equilibrium of alkane−alkanol mixtures (Kerber and Kehlen, 1990), to bubble- and dew-point calculations for polydisperse hydrocarbon mixtures (Massanetz et al., 1990), and to liquid−liquid polymer solution fractionation (Ratzsch et al., 1991). Sandler and Libby (1991) elucidated how distributions satisfy equilibrium relations and mass balances.

Purification of an homologous polymer mixture by removing low MW components from the distribution was required for polymer degradation experiments by Madras et al. (1996). Purification was accomplished by precipitating higher-MW molecules by slow addition of poorer solvent to polymer solution. Precipitated polymer (gel phase) remains in contact with the solution (sol phase). In the absence of inefficiencies, such as physical entrapment of polymer in aggregates (Francuskiewicz, 1994), the system is always at equilibrium. The solution goes through a cloud point, where polymer just begins to precipitate, and can be extended until the last low-MW polymer precipitates. The process is a finite rather than a differential separation, such as batch distillation, for which the vapor is removed and condensed so that the liquid is always at its bubble point. For batch precipitation the precipitate would be removed as it forms. Batch, time-dependent distillation is usually modeled with a discrete rather than a continuous mixture (Treybal, 1980). Mass balances, combined with phase equilibrium ratios, allow a numerical solution for the discrete compounds as a function of time. When hundreds or thousands of homologous macromolecules with different MWs comprise a MWD, a continuous-mixture approach is more convenient.

MWDs obey mass-balance (population-balance) equations, which sometimes can be solved exactly for the distribution. More frequently, the population balance is solved approximately, either numerically or for the first few moments. For fractionation of polydisperse systems, we show that following the Flory-Huggins theory by using phase-equilibrium partition coefficients (Flory, 1953; Huggins and Okamoto, 1967) provides a convenient basis for solving the population balances. Although either discrete or continuous distributions can describe polydispersity, computations are frequently easier for continuous functions. For polymers with continuous MWDs, the partition coefficients will also be continuous over the range of MW or other distributed property. This leads to the often-stated condition that polymer fractionation is never sharp, and homologous macromolecules are always polydisperse in the separated phases. The numerous applications, as well as the mathematical and thermodynamic complexities, justify the recent resurgence of interest in phase-equilibrium separations in polydisperse systems.

Our objectives are to propose a unified approach to continuous-mixture separations, and to present models that apply to both sol−gel and vapor−liquid fractionations. After defining distributions and their moments, we introduce the partition coefficient and derive mass-balance equations for finite (flash) and for differential fractionations. One differential fractionation with a particular partition coefficient has a similarity solution. Given reasonable partition coefficient expressions, exact solutions can be derived that have advantages over moment solutions.

Background

For nonreactive separation processes, it is convenient to define normalized distributions $p(x,t)$

$$p(x,t) = P(x,t)/N(t), \tag{1}$$

where $N(t)$ is the total number of moles at time t and $P(x,t)dx$ is the number of moles in the property range $(x, x+dx)$. Moments are defined as

$$P^{(n)}(t) = \int dx\, x^n P(x,t), \tag{2}$$

where the integral is over the entire range of x. If x is MW (the usual case for polymers), then for $n = 0$ and 1 the moments are moles $N(t)$ and mass, respectively. The relationship between distribution moments and their normalized counterparts is $P^{(n)}(t) = N(t)p^{(n)}(t)$. Moments of $p(x, t)$ are unity for $n = 0$, and number average molecular weight M_n for $n = 1$. The mass-average molecular weight is $M_w = P^{(2)}/P^{(1)} = p^{(2)}/p^{(1)}$.

Consider an equilibrium fractionation of an initial phase into two phases denoted by subscripts g and s (for example, vapor and liquid, or gel and sol). If $P_o(x)$ is the initial distribution, the material balance holds for each MW x at each time t

$$P_o(x,t) = P_g(x,t) + P_s(x,t). \tag{3}$$

The nth-order moments are conserved

$$P_o^{(n)}(t) = P_g^{(n)}(t) + P_s^{(n)}(t), \tag{4}$$

and thus

$$N_o p_o^{(n)} = N_g p_g^{(n)} + N_s p_s^{(n)}. \tag{5}$$

Since zeroth moments of $p(x)$ are unity, it follows that $N_o(t) = N_g(t) + N_s(t)$, or in terms of mole fractions, $1 = X_g + X_s$.

The equilibrium between two partitioned phases can be represented by an equilibrium ratio of the two normalized distributions, which are intensive thermodynamic quantities (Cotterman et al., 1985)

$$K(x,t) = p_g(x,t)/p_s(x,t). \tag{6}$$

Such partitioning relations are the result of equating the chemical potentials in each phase for each species with property x (Cotterman and Prauznitz, 1985; Flory, 1953). The Flory-Huggins theory for polymer solutions (Flory, 1953; Huggins and Okamoto, 1967), which is an approximate model often used as the starting point for more sophisticated models (Munk, 1989), specifies that

$$K(x) = K_0 \exp(\sigma x). \tag{7}$$

For $\sigma > 0$ the subscript g represents the higher-MW phase (gel), whose solubility decreases with MW. For $\sigma < 0$, g is the lower-MW phase (vapor), whose volatility decreases with MW increase. The exponential function can be expanded

$$\exp(z) = 1 + z/1! + z^2/2! + z^3/3! + \cdots, \tag{8}$$

and with $z = \sigma x$ the truncated series is a polynomial (Sezgi et al., 1998)

$$\begin{aligned} K(x) &= K_0\left(1 + \sigma x/1! + \sigma^2 x^2/2! + \sigma^3 x^3/3! + \cdots\right) \\ &= K_0\left(1 + \textstyle\sum_{j=1} b_j x^j\right), \end{aligned} \tag{9}$$

where $b_j = \sigma^j/j!$.

Finite Fractionation

Exact equilibrium calculations are straightforward when Eqs. 3 and 6 are combined by eliminating p_g

$$p_s(x) = p_o(x)/\left[X_s + X_g K(x)\right], \tag{10}$$

where $X_s = N_s/N_o = 1 - X_g$. Substituting the polynomial (Eq. 9) into the equilibrium relation (Eq. 6) and applying the moment operation (Eq. 2) yields

$$p_g^{(n)} = K_0\left(p_s^{(n)} + \Sigma_{j=1} b_j p_s^{(n+j)}\right). \tag{11}$$

When $p_g^{(n)}$ is eliminated from the moment balance (Eq. 5), one obtains

$$p_o^{(n)} = \left(X_g K_0 + X_s\right) p_s^{(n)} + X_g K_0 \Sigma_{j=1} b_j p_s^{(n+j)}. \tag{12}$$

Unless recurrence relations for moments can be found, the moment hierarchy requires closure by truncation of the summation to calculate a moment at any order. A subsequent computation with truncation at the next higher order would confirm that neglected expansion terms are truly negligible. If the series converges slowly, many terms may be required for an accurate solution. If the distributions are to be reconstructed from the moments (Sezgi et al., 1998), an expansion in orthogonal polynomials may be necessary. For the special case that all phases can be approximated by Γ-distributions or other three-parameter distributions, only the first three moments would be needed (McCoy and Madras, 1998). Compared to the exact computation, the moment approximation, although straightforward, is laborious.

The exact approach is valid when the functions $K(x)$, $p_s(x)$, and $p_g(x)$ consistently satisfy the mass balance and equilibrium relation. The corresponding condition for discrete vapor–liquid fractionation requires the equilibrium ratio to satisfy mass balances at the process temperature and pressure. Some of the K values must be less than unity and others must be greater than unity. Normalization of $p_s(x)$ and $p_g(x)$ requires that

$$\int dx\, p_s(x) = 1 \tag{13}$$

and

$$\int dx\, K(x) p_s(x) = 1. \tag{14}$$

A straightforward procedure is to consider that $p_s(x)$ is given, and to compute an expression for K_0 by Eq. 14. Then $p_g(x) = K(x) p_s(x)$, and the mass balance (Eq. 10) gives $p_o(x)$. All the moments will then obey the mass balance. With a normalized Γ-distribution

$$p_s(x) = 1/[\beta\Gamma(\alpha)](x/\beta)^{\alpha-1}\exp(-x/\beta), \tag{15}$$

and for the exponential equilibrium ratio (Eq. 7), Eq. 14 requires that

$$K_0 = (1 - \sigma\beta)^{\alpha}. \tag{16}$$

In general the initial distribution, $p_o(x)$, will not be of the same functional form as the product distributions, $p_s(x)$ and $p_g(x)$. Sandler and Libby (1991) discussed and demonstrated this important point through calculations for hydrocarbon fractionations. When the initial and vapor distributions were exponential, the liquid distribution was not a simple exponential.

Given the initial distribution, the mass balance (Eq. 10) and the integrations of Eqs. 13 and 14 provide two algebraic equations for two parameters, and therefore the two equilibrium distributions are determined. If σ is given, then K_0 and X_s can be determined, or if X_s is given, then K_0 and σ can be determined. Although closed expressions for the two parameters are not possible for realistic expressions of $p_o(x)$ and $K(x)$, numerical solutions to the algebraic equations are feasible.

To illustrate computations of phase-equilibrium fractionations, we consider a Γ-distribution (Eq. 15) with $\beta = 2 \times 10^4$ g/mol, $\alpha = 9$, $X_s = 0.45$ (Figure 1). The parameter σ in the equilibrium ratio (Eq. 7) determines the position of the two equilibrium distributions on the x-axis. Larger σ splits the phases, yielding better separation. In Figures 1A and 1B we have $\sigma = 2 \times 10^{-5}$ and 1×10^{-6}, respectively. When $K(x)$ is linear for sufficiently small σx (Figure 1B), the distributions have nearly the same functional form, but poor separation is achieved. If the initial distribution is sufficiently narrow, $K(x)$ can be approximated as linear and the fractionated equilibrium phases are not widely separated. When moments are used to construct the g and s distributions, the comparison with the exact solution is favorable only when σx is small, that is, when $K(x)$ is effectively linear.

Cloud points are defined when the smallest amount of the second phase appears, for example, at the point of first turbidity during titration of a polymer solution by dropwise ad-

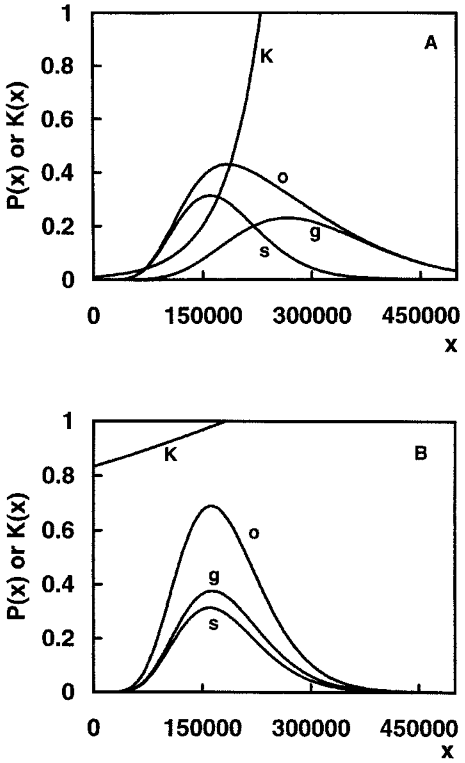

Figure 1. Initial distribution, $P_o(x)$, fractionates into two phases, $P_g(x)$ and $P_s(x)$, according to the equilibrium ratio, $K(x) = (1 + \sigma\beta)^{\alpha}$ exp $(-\sigma x)$.

(A) $\sigma = 2 \times 10^{-5}$ and (B) $\sigma = 1 \times 10^{-6}$; $P_s(x)$ is a Γ-distribution with $\beta = 2 \times 10^4$, $\alpha = 9$, $X_s = 0.45$.

dition of a less effective solvent. For vapor–liquid equilibrium the dew point is the limit when X_s approaches zero, so that $P_g(x) \approx P_o(x)$. The bubble point is the limit as X_g approaches zero, so that $P_s(x) \approx P_o(x)$. Bubble point moments ($X_s = 1$) can be represented as

$$p_g^{(n)} = K_0\left(p_0^{(n)} + \Sigma_{j=1} b_j p_o^{(n+j)}\right). \tag{17}$$

The separation of a continuously distributed population into different phases was addressed recently by Evans et al. (1998), who derived a simple relationship among the moments of the initial distribution and its separated equilibrium phases. For the case of a narrow initial distribution and slightly perturbed equilibrium, it was shown that the difference in moments of the separated phases is proportional to the next higher-order moment of the initial phase (Fredrickson, 1998). Our general approach shows clearly the restrictions on the result. Following Evans et al. (1998), one can form the difference between moments of the g and s phases when the equilibrium ratio is linear in x

$$p_s^{(n)} - p_g^{(n)} = (1 - K_0)\, p_o^{(n)} + K_0 \sigma p_o^{(n+1)}. \tag{18}$$

According to Eq. 16, if σ is small, then $K_0 \approx 1$ and it follows that

$$p_s^{(n)} - p_g^{(n)} = \sigma p_o^{(n+1)}, \tag{19}$$

which is the result proposed by Evans et al. (1998) by a statistical thermodynamics argument. The derivation emphasizes the constraints of the result. The parent distribution must be narrow (relative to the slope of the equilibrium ratio), or the equilibrium ratio must be linear in x. Also, the equilibrium must refer to a cloud point, that is, one of the daughter phases must be present in a negligible amount.

To extend finite fractionation calculations to multiple phases (Evans, 1999), one would form the equilibrium partition ratios for each phase pair. Existence of such equilibrium ratios is a consequence of the thermodynamic requirement that chemical potentials are equal at each value of x for all phases in equilibrium. The same disadvantages of moment representation obviously apply to multiphase equilibrium.

The extension to multivariable distributions can also be made. If distributions depend on two variables, x and y, they can be pictured as three-dimensional plots for $p_o(x,y)$, $p_g(x,y)$, and $p_s(x,y)$. Equilibrium constants are defined by $K(x,y) = p_g(x,y)/p_s(x,y)$, for example, $K(x,y) = K_o \exp(-ax - by)$.

Differential Fractionation

When the separated equilibrium phase is removed as soon as it is formed, the fractionation requires description by differential mathematics. A common example in chemical separations is batch (differential) distillation, in which the vapor in equilibrium with the liquid is continuously condensed and collected separately (Treybal, 1980). The usual treatment is for *discrete* mixtures of species i with mole fractions x_i and y_i in the liquid and vapor phases, respectively. If the molar flow rate of vapor leaving the liquid surface is dN_g/dt, then the loss rate from the liquid is

$$dN_s/dt = -\, dN_g/dt. \tag{20}$$

The mass (mole) balance on species i is

$$d(x_i N_s)/dt = -\, y_i\, dN_g/dt. \tag{21}$$

The initial conditions are $N_s(t=0) = N_o$ and $N_g(t=0) = 0$. Eliminating N_g and rearranging gives after integration

$$\int_{x_{io}}^{x_i} dx_i/(y_i - x_i) = \ln(N_s/N_o). \tag{22}$$

The integral can be evaluated numerically if an equilibrium relation $K_i = y_i/x_i$ is substituted. When the time dependency of the equilibrium ratio is expressed in terms of the separation progress represented by $N_s(t)$, eliminating y_i yields

$$x_i/x_{io} = (N_o/N_s) \exp\left(\int_{N_o}^{N_s} K_i\, d(\ln N_s')\right), \tag{23}$$

where the prime (′) denotes the integration variable, which is bounded by N_o and $N_s = 0$.

For *continuous* mixtures the molar balance (Eq. 21) is expressed in terms of the distributions,

$$d(p_s N_s)/dt = -\, p_g\, dN_g/dt. \tag{24}$$

Substituting the overall mole balance (Eq. 20) and the equilibrium relation (Eq. 6) yields the differential equation

$$d \ln p_s/dt = (K - 1)\, d \ln N_s/dt. \tag{25}$$

When the partition coefficient is a function of x and N_s, where $N_s(t)$ provides the time dependence, integration gives

$$p_s(x) = p_o(x)(N_o/N_s) \exp\left[\int_{N_o}^{N_s} K\, d(\ln N_s')\right]. \tag{26}$$

The similarity to the discrete case (Eq. 23) is obvious. The differential fractionation result (Eq. 26) is consistent with the finite fractionation result (Eq. 10) if only slight separation occurs. For example, at the cloud point, where $N_o \approx N_s$, the integral in Eq. 26 gives $K(1 - N_o/N_s)$, a small number that allows the reciprocal exponential to be expanded to first order, yielding Eq. 10. Of course, the dependence of K and N will be different for time-dependent differential fractionation and for path-independent finite fractionation.

The separated phase can be either (a) high MW, as in precipitation from solution or condensation of a vapor, or (b) low MW, as in dissolution of a solid polymer or vaporization of a liquid. The governing equations represented by (a) and (b) can readily be formulated. During the process the thermodynamic state is altered, for example, by changing the temperature or the solvent efficacy. The change in thermodynamic state with time will be accompanied by a change in the value of K and a corresponding change in the number of moles in each phase, so the change with time can be represented by assuming the equilibrium ratio to depend on $N(t)$. If the partition coefficient K has the same definition for (a) and (b), then the dependence on x will be inverted, but the N dependence will be the same. The separate N and x dependencies of the partition coefficient, valid for the Flory-Huggins model and hence a reasonable assumption for more complex models, facilitate calculations. For a fractionation process in which $N_s(t=0) = N_o$ and $N_s(t \to \infty) \to 0$, analytical solutions are possible when the x and N dependencies are represented as the product

$$K(x,N_s) = f(x)/N_s^m \qquad \text{for } (a), \tag{27a}$$

$$= f(x)^{-1}/N_s^m \qquad \text{for } (b). \tag{27b}$$

When the integral in Eq. 26 is done, we can write the result as

$$p_s(x)N_s\phi_s = p_o(x)N_o\phi_o, \tag{28}$$

where for (a) $\ln \phi = f(x)/mN^m$ and for (b) $\ln \phi = f(x)^{-1}/mN^m$ with subscript s or o on N and ϕ. If $m=0$ the integration (Eq. 26) yields (a) $\phi = N^{-f(x)}$ and for (b) $\phi = N^{-1/f(x)}$. The differential amounts of *removed* phase can be collected together and satisfy the mass balances at any time, $N_g p_g(x) = N_o p_o(x) - N_s p_s(x)$ and $N_g = N_o - N_s$. As the differential fractionation approaches completion, $N_s \to 0$, $p_s(x) \to 0$, and therefore $p_g(x) \to p_o(x)$, so that the initial polymer is totally recovered as precipitate.

Two versatile functional forms for $f(x)$ can at least semi-quantitatively describe physical realities. One possibility is to let $f(x) = \kappa x^\lambda$. Evolving distributions (Eq. 28) with $m=1$ are plotted in Figure 2 for precipitation (a) and in Figure 3 for the dissolution (b) of a polymer. Case (a) has the added interest that for an initial generalized Γ-distribution and $m=1$, the solution is a *similarity* solution, that is, the time dependence is determined solely by $\beta(t)$ in the group x^λ/β. We follow arguments similar to Ziff (1991) and McCoy and Madras (1998) to demonstrate the equivalence. Consider that the differential equation (Eq. 25) is satisfied by the generalized Γ-distribution (normalized to unity)

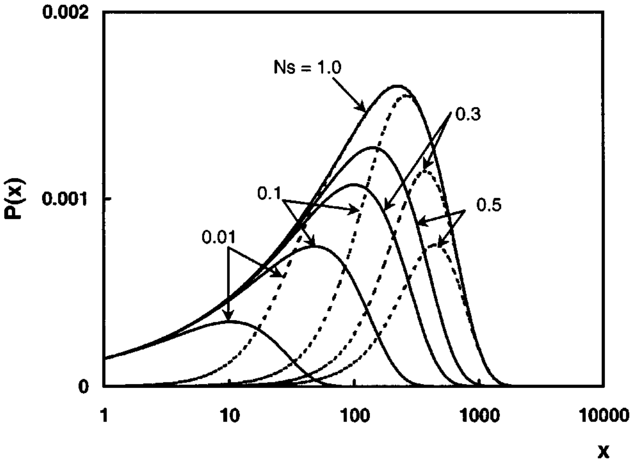

Figure 2. Evolving distributions for differential fractionation (precipitation from solution) when $K(x,N) = \kappa x^\lambda/N$, with $\kappa = 10^{-4}$.

The initial distribution is a generalized Γ-distribution, with $\lambda = 1.5$, $N_o = 1$, $\beta_o = 10^4$, $\alpha = 2 - 1/\lambda$. Solid lines are solution distributions and dashed lines are total precipitate distributions for $N_s = 0.01, 0.1, 0.3, 0.5, 1.0$.

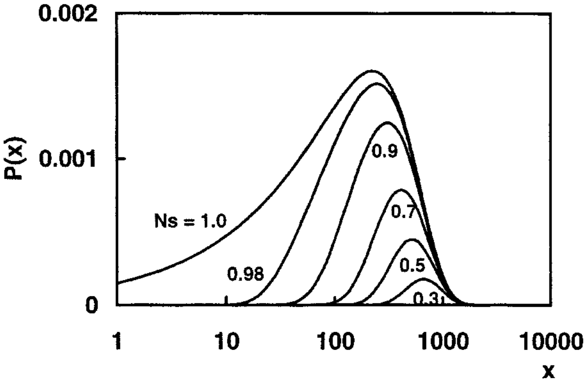

Figure 3. Evolving distributions for differential fractionation (dissolution of undissolved polymer) when $K(x,N) = 1/(\kappa x^\lambda N)$ with $\kappa = 10^{-4}$.

The initial distribution is the same as in Figure 2.

$$p_s(x,t) = \frac{(\lambda/\beta^{1/\lambda})(x^\lambda/\beta)^{\alpha-1}}{\Gamma(\alpha-1+1/\lambda)}\exp(-x^\lambda/\beta), \tag{29}$$

where $\Gamma(\alpha+1) = \alpha\Gamma(\alpha)$ is the Γ-function. For $\lambda = 1$, Eq. 29 is a Γ-distribution, Eq. 15. The initial condition is Eq. 29 with subscript o on p and β. The time derivative of the logarithm of $p_s(x,t)$ in Eq. 29 simplifies to

$$d\ln p_s/dt = (d\ln\beta/dt)(1-\alpha-1/\lambda+x^\lambda/\beta), \tag{30}$$

which is substituted into Eq. 25 with $K = \kappa x^\lambda/N_s$. We next equate coefficients of powers of x. When $\alpha = 2 - 1/\lambda$, the result gives the β dependence on $N_s(t)$

$$\beta = \beta_o - \kappa(N_o - N_s)(\beta_o/N_o)^2 \tag{31}$$

and

$$N_s/\beta = N_o/\beta_o. \tag{32}$$

The solution for the distribution can be written as

$$P_s(x,t) = N_s(\lambda/\beta^{1/\lambda})(x^\lambda/\beta)^{1-1/\lambda}\exp(-x^\lambda/\beta). \tag{33}$$

This is equivalent to the solution plotted in Figure 2, which can be proved by substituting p_o from Eq. 29 into Eq. 28, and using Eqs. 31 and 32. If the initial distribution were different from Eq. 29, the method of McCoy and Madras (1998) would show how α evolves with time to the constant value $2 - 1/\lambda$.

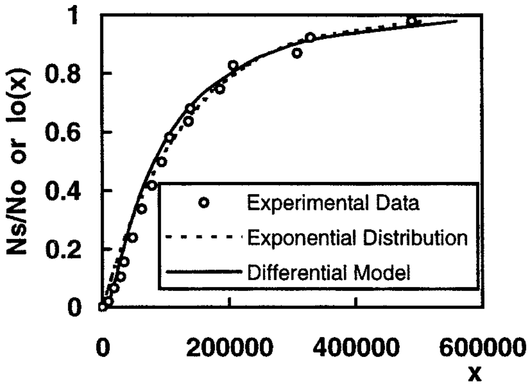

Figure 4. Comparison to experimental data (Okamoto and Sekikawa, 1961) of differential fractionation model with $K(x) = \exp(\sigma x)$ and $\sigma = 5.0 \times 10^{-6}$.

If instead we let $f(x) = \exp(\sigma x)$ and $m = 0$ in Eqs. 27, then $K(x) = \exp(\sigma x)$ (Flory, 1953; Kamide, 1977), and the results of precipitation and dissolution calculations are similar to Figures 2 and 3. Figure 4 is a comparison of the model to experimental data (Table II of Okamoto and Sekikawa, 1961) for polyethylene in xylene successively precipitated by adding polyethylene glycol. The data are given as a cumulative distribution

$$I_o(x) = \int_0^x p_o(x)\, dx, \tag{34}$$

and are well approximated by $I_o(x) = 1 - \exp(-x/\beta_o)$ with $\beta_o = 1.30 \times 10^5$. The distribution $p_o(x)$ is a Γ-distribution with $\alpha = 1$, which is identical to an exponential (most probable) distribution, $p_o(x) = (1/\beta_o)\exp(-x/\beta_o)$. The experimental procedure yielded 16 fractions, which were evidently enough to approximate a differential fractionation having an infinite number of fractions. Because each precipitate fraction is polydisperse, we calculate the number average MW of $p_g(x) = K(x)p_s(x)$ as

$$x_{\text{avg}} = \int_0^\infty e^{\sigma x} p_s(x)\, x\, dx, \tag{35}$$

where $p_s(x)$ is given by Eq. 28 and $m = 0$ and $f(x) = \exp(\sigma x)$ in Eq. 27a. Equation 28 becomes

$$p_s(x) N_s^{1-\exp(\sigma x)} = p_o(x) N_o^{1-\exp(\sigma x)}. \tag{36}$$

The amount of polymer of MW less than x_{avg} is N_s. Simpson's rule integration gives x_{avg} as a function of N_s/N_o, which is equivalent to $I_o(x)$ for the fractionation process. Figure 4 shows that $\sigma = 5.0 \times 10^{-6}$ provides satisfactory agreement with the data.

Conclusions

Phase equilibrium fractionations for many-component systems have numerous applications in polymer and petrochemical engineering. Usually, homologous mixtures with many components can be represented as continuous distributions in a variable x, for example, molecular weight (MW). Continuous distributions have partition ratios that are also continuous, leading to distributions in the separated phases. Fractionated continuous mixtures are thus always polydisperse. We have shown that analysis of fractionation for multicomponent homologous mixtures is facilitated if an equilibrium partition ratio in terms of property x, $K(x) = p_g(x)/p_s(x)$, can be postulated. The approximate Flory-Huggins model for dilute polymer solutions leads to exponential dependence of K on x, but other forms of $K(x,t)$ may be applicable under different conditions. Given the partition coefficient, we have shown how finite (flash) fractionations can be computed exactly, without the need for approximate moment methods. The treatment clarifies how mass balance and phase equilibrium interrelate for multicomponent systems.

For differential (batch) fractionation a parameter such as the number of moles remaining in the batch (N_s) represents the extent of separation and can be used as a measure of time. Analytical solutions are possible when the x and N_s dependencies of the partition coefficient are in product form, $K(x,N) = f(x)/N^m$, which generalizes the Flory-Huggins model. A power-law dependence on x yields a similarity solution for the MWD for differential fractionation. Exponential partitioning provides agreement with experimental cumulative distribution data from the literature. Results derived for finite and differential fractionations are applicable to vapor–liquid or gel–sol systems.

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