Oligomer Compatibility by Continuous Thermodynamics

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OLIGOMER COMPATIBILITY BY CONTINUOUS THERMODYNAMICS

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ABSTRACT

To describe the details of the liquid-liquid equilibrium of oligomer mixtures, it is essential to use Gibbs free energy functions generalizing the classical Flory Huggins relation by replacing Huggins' χ-term by a function depending on the averages of the molecular weight distributions. In this paper the concept of continuous thermodynamics is applied to establish a simple calculation procedure for the number-average segment number. Instead of the well-known sums with respect to the species, integrals occur which, in the case of Schulz-Flory distributions, may be calculated analytically, leading to simple formulas for the cloud-point curve and the shadow curve. The method is applied to model calculations showing that the chosen Gibbs free energy function may account for the details of the liquid-liquid equilibrium of oligomer mixtures and to a real oligomer system taken from the literature.

INTRODUCTION

The cloud-point curve of polymer mixtures usually possesses a relatively simple shape. However, for mixtures of oligomers this curve often exhibits features like asymmetry, shoulders, or two extrema. Similar statements apply to the spinodal curve.

To understand such curves, an appropriate expression for the Gibbs energy is needed. Generalizing the classical Flory-Huggins relation, the change of Gibbs free energy of mixing $\Delta_M \bar{\bar{G}}$ per mole of segments for polymer systems or oligomer systems can be written as

$$\Delta_M \bar{\bar{G}} = RT \sum_i \frac{\psi_i}{r_i} \ln \psi_i + \bar{\bar{G}}^E. \tag{1}$$

Here R is the gas constant, T is the temperature, r_i is the segment number, and ψ_i is the segment fraction. The sum is to be extended over all species i present in the mixture. The quantity $\bar{\bar{G}}^E$ is called the segment-molar excess Gibbs free energy. It generalizes the χ-term of the Flory-Huggins relation so as to account for more sophisticated Gibbs free energy expressions.

For describing the features of oligomer mixtures, different $\bar{\bar{G}}^E$ relations were applied, such as the extended Huggins concept [1], the free volume theory [2], or replacement of the χ-parameter by a quadratic function of the segment fraction [3]. In all these cases, $\bar{\bar{G}}^E$ is assumed to be independent of the molecular weight distributions (MWD) of the oligomers involved. Therefore, $\bar{\bar{G}}^E$ is also not influenced by the transition from oligomers to polymers or vice versa. However, the $\bar{\bar{G}}^E$ function is crucial for describing the liquid-liquid phase equilibrium. Thus, the discussed independence means that the Gibbs free energy functions mentioned are unable to account for the essential changes of the liquid-liquid equilibrium being connected with the transition between polymers and oligomers.

Hence, $\bar{\bar{G}}^E$ functions have to be used that depend on the MWD of the polymers or oligomers considered. Koningsveld et al. [3] applied Silberberg's entropy-of-mixing expression to calculate spinodals. However, on account of the complexity of this expression, the more complicated calculation of cloud-point curves and shadow curves would be very computer-intensive for the polydisperse case.

In this paper another $\bar{\bar{G}}^E$ relation is used that depends on the MWD by means of the number average of the segment number. Cloud-point curves, shadow curves, spinodals, and critical points of oligomer mixtures will be calculated.

The calculation of the cloud-point curves and shadow curves is very much simplified by applying the method of continuous thermodynamics [4-7]. This method consists in using the continuous distribution density functions

directly (i.e., without arbitrary splitting into pseudocomponents) within the framework of thermodynamics. Accordingly, the well-known sums of traditional thermodynamics are replaced by integrals which may be calculated analytically for Schulz-Flory distributions. In this way simple closed formulas which are easy to handle are obtained instead of the usual sums which have to be calculated numerically.

LIQUID-LIQUID EQUILIBRIUM

The chemical potential forms the starting point for consideration of phase equilibria. According to Eq. (1), the chemical potential $\bar{\bar{\mu}}_i$ of a species i per mole of segments reads

$$\bar{\bar{\mu}}_i = \bar{\bar{\mu}}_i^*(T,P) + RT \left[\frac{1}{r_i} \ln \psi_i + \frac{1}{r_i} - \frac{1}{\bar{r}_n} \right] + RT \ln \bar{\bar{\gamma}}_i. \tag{2}$$

The first term on the right-hand side is the chemical potential of the pure species i, and $\bar{r}_n$ is the number-average segment number for all species in the mixture. The term $RT \ln \bar{\bar{\gamma}}_i$ generalizes the χ-term in the classical Flory-Huggins $\bar{\bar{\mu}}_i$ relation. The quantity $\bar{\bar{\gamma}}_i$ is called the segment-molar activity coefficient and may be calculated from $\bar{\bar{G}}^E$.

In applying continuous thermodynamics, the species of a polydisperse polymer or oligomer B are identified by a continuous variable, i.e., the molecular weight M instead of the discrete index i. The relation for the chemical potential per mole of segments reads [5]

$$\bar{\bar{\mu}}_B(M) = \bar{\bar{\mu}}_B{}^0(M,T,P) + RT \left[\frac{1}{r_B(M)} \ln \psi_B W_B(M) + \frac{1}{r_B(M)} - \frac{1}{\bar{r}_n} \right] +$$

$$RT \ln \bar{\bar{\gamma}}_B(M). \tag{3}$$

The segment fractions ψ_i of the discrete species i are replaced in continuous thermodynamics by the product $\psi_B W_B(M)$ where ψ_B is the overall segment fraction of the polymer or oligomer B and $W_B(M)$ is the distribution density function defined by the statement that $W_B(M)dM$ is the relative segment fraction of all B-species with molar masses between M and $M + dM$. Hence,

$$\int W_B(M)dM = 1. \tag{4}$$

The integral is to be taken over the entire M range. Furthermore, the transition to continuous thermodynamics leads to including an additional term in the concentration-independent reference term $\bar{\mu}_B{}^0(M,T,P)$ [5].

In continuous thermodynamics the equilibrium condition between two phases $'$ and $''$ for systems containing two polydisperse polymers or oligomers B and C reads

$$\bar{\mu}_B{}'(M) = \bar{\mu}_B{}''(M)$$

$$\bar{\mu}_C{}'(M) = \bar{\mu}_C{}''(M) \tag{5}$$

These conditions are valid for the total range of M values. The relation for $\bar{\mu}_C(M)$ is obtained by substituting C for B in Eq. (3); $\psi_B + \psi_C = 1$.

The mathematical problem involved in Eqs. (5) depends on the expressions for $\bar{\gamma}_B(M)$ and $\bar{\gamma}_C(M)$ resulting from the applied $\bar{\bar{G}}^E$ model. If $\bar{\bar{G}}^E$ does not depend on the distribution density functions, $W_B(M)$ and $W_C(M)$, then $\bar{\gamma}_B$ and $\bar{\gamma}_C$ are also independent of these functions and, furthermore, they do not depend on M. This is the case for the simple Huggins χ concept ($c = d = 0$ in Eqs. 6 and 7) and for its generalization by substituting a quadratic ψ_B polynomial for χ:

$$\frac{\bar{\bar{G}}^E}{RT} = \beta(T)\psi_B(1 - \psi_B)[1 + c\psi_B + d\psi_B{}^2], \tag{6}$$

$$\ln \bar{\gamma}_B = \beta(T)(1 - \psi_B)^2 [1 + 2c\psi_B + 3d\psi_B{}^2],$$

$$\ln \bar{\gamma}_C = \beta(T)\psi_B{}^2 [1 - c + 2(c - d)\psi_B + 3d\psi_B{}^2]. \tag{7}$$

If, however, $\bar{\bar{G}}^E$ depends on $W_B(M)$ and $W_C(M)$, the segment-molar activity coefficients $\bar{\gamma}_B$ and $\bar{\gamma}_C$ depend also on $W_B(M)$ and $W_C(M)$, and they are actually functions of M. An example is provided by the $\bar{\bar{G}}^E$ model mainly used in this paper,

$$\frac{\bar{\bar{G}}^E}{RT} = \beta(T)\psi_B(1 - \psi_B) \frac{1 + Q/\bar{r}_n}{1 - \gamma\psi_B} \tag{8}$$

This relation is similar in some respect to a relation used by Kennedy, Gordon, and Koningsveld [8] for considering polymer solutions. Here, $\bar{\bar{G}}^E$ depends on the distribution density functions since $\bar{r}_n$ is given by

$$\frac{1}{\overline{r}_n} = \frac{\psi_B}{\overline{r}_{n,B}} + \frac{\psi_C}{\overline{r}_{n,C}} \ ; \quad \frac{1}{\overline{r}_{n,B}} = \int \frac{W_B(M)}{r_B(M)} \, dM; \quad \frac{1}{\overline{r}_{n,C}} = \int \frac{W_C(M)}{r_C(M)} \, dM. \quad (9)$$

The relations for $\overline{\overline{\gamma}}_B$ and $\overline{\overline{\gamma}}_C$ read

$$\ln \overline{\overline{\gamma}}_B(M) = \beta(T) \left\{ \frac{(1 - \psi_B)^2}{(1 - \gamma\psi_B)^2} \left[1 + \frac{Q}{\overline{r}_n} \right] + \frac{\psi_B(1 - \psi_B)}{1 - \gamma\psi_B} \, Q \left[\frac{1}{r_B(M)} - \frac{1}{\overline{r}_n} \right] \right\},$$

$$\ln \overline{\overline{\gamma}}_C(M) = \beta(T) \left\{ \frac{\psi_B^2(1 - \gamma)}{(1 - \gamma\psi_B)^2} \left[1 + \frac{Q}{\overline{r}_n} \right] + \frac{\psi_B(1 - \psi_B)}{1 - \gamma\psi_B} \, Q \left[\frac{1}{r_C(M)} - \frac{1}{\overline{r}_n} \right] \right\}.$$

$$(10)$$

Applying Eqs. (3) and (10), the phase equilibrium condition, Eq. (5), results in

$$W_B''(M) = \frac{\psi_B'}{\psi_B''} \, W_B'(M) \exp \left[\sigma_B + \tau_B r_B(M) \right] \quad (11)$$

with

$$\sigma_B = -\beta(T)Q \left[\frac{\psi_B''(1 - \psi_B'')}{1 - \gamma\psi_B''} - \frac{\psi_B'(1 - \psi_B')}{1 - \gamma\psi_B'} \right], \quad (12)$$

$$\tau_B = \frac{1}{\overline{r}_n''} - \frac{1}{\overline{r}_n'} - \beta(T) \left\{ \frac{(1 - \psi_B'')^2}{(1 - \gamma\psi_B'')^2} \left[1 + \frac{Q}{\overline{r}_n''} \right] - \frac{\psi_B''(1 - \psi_B'')}{1 - \gamma\psi_B''} \frac{Q}{\overline{r}_n''} \right.$$

$$\left. - \frac{(1 - \psi_B')^2}{(1 - \gamma\psi_B')^2} \left[1 + \frac{Q}{\overline{r}_n'} \right] + \frac{\psi_B'(1 - \psi_B')}{1 - \gamma\psi_B'} \frac{Q}{\overline{r}_n'} \right\}, \quad (13)$$

and analogous relations for the ensemble C.

Considering the composition of the phase $'$ (i.e., ψ_B', $W_B'(M)$, $W_C'(M)$) and the pressure P to be specified, the function $T(\psi_B')$ describes the cloud-point curve, and the function $T(\psi_B'')$ describes the shadow curve. Hence, Eq. (11) and the corresponding relation for the polymer or oligomer C provide immediately the distribution density functions $W_B''(M)$ and $W_C''(M)$ of

the newly formed phase $''$. These relations still contain the three unknowns of the problem: T, ψ_B'', and $\bar{r}_n''$. For their determination, three equations are needed which result from Eq. (4) applied to $W_B''(M)$ and $W_C''(M)$ and from Eq. (9) applied to phase $''$. Using Eq. (11) and the corresponding relation for the polydisperse ensemble C, these equations read

$$\psi_B'' = \int \psi_B' W_B'(M) \exp \left[\sigma_B + \tau_B r_B(M)\right] dM, \tag{14}$$

$$1 - \psi_B'' = \int (1 - \psi_B') W_C'(M) \exp \left[\sigma_C + \tau_C r_C(M)\right] dM, \tag{15}$$

$$\frac{1}{\bar{r}''} = \int \frac{\psi_B' W_B'(M)}{r_B(M)} \exp \left[\sigma_B + \tau_B r_B(M)\right] dM$$

$$+ \int \frac{(1 - \psi_B') W_C(M)}{r_C(M)} \exp \left[\sigma_C + \tau_C r_C(M)\right] dM. \tag{16}$$

In the general case the integrals have to be calculated numerically. If, however, the distribution density functions for the polymers or oligomers B and C in the given phase $'$ are Schulz-Flory distributions, i.e., if the relation

$$W_B' = \frac{k_B}{\bar{r}'_{n,B}\, \Gamma(k_B)} \left(\frac{r_n}{\bar{r}'_{n,B}}\right) \exp \left(-k_B \frac{r_B}{\bar{r}'_{n,B}}\right) \tag{17}$$

and an analogous relation for W_C' apply, all integrations in Eqs. (14)-(16) may be performed analytically. In Eq. (17), $\bar{r}'_{n,B}$ and k_B are the parameters of the distribution, and Γ is the Γ function. Assuming $\bar{r}'_{n,B}\tau_B/k_B < 1$ and $\bar{r}'_{n,C}\tau_C/k_C < 1$, Eqs. (14)-(16) result by analytical integration in

$$\psi_B'' = \psi_B' \left(1 - \frac{\bar{r}'_{n,B}\tau_B}{k_B}\right)^{-(k_B+1)} \exp \sigma_B, \tag{18}$$

$$1 - \psi_B'' = (1 - \psi_B') \left(1 - \frac{\bar{r}'_{n,C}\tau_C}{k_C}\right)^{-(k_C+1)} \exp \sigma_C, \tag{19}$$

$$\frac{1}{\bar{r}_n''} = \frac{\psi_B''}{\bar{r}_{n,B}'} \left(1 - \frac{\bar{r}_{n,B}' T_B}{k_B}\right)^{-k_B} \exp \sigma_B$$

$$+ \frac{(1 - \psi_B')}{\bar{r}_{n,C}'} \left(1 - \frac{\bar{r}_{n,C}' T_C}{k_C}\right)^{-k_C} \exp \sigma_C. \tag{20}$$

STABILITY

Investigations of phase stability lead to equations for the spinodal (i.e., the limit of instability) and the critical point. In the framework of this paper, the traditional Gibbs ideas for treating the critical state are applied and the details for the direct surroundings of a critical point (compare, e.g., Ref. 9) are not accounted for. The considerations may be applied to the discrete as well as to the continuous basis.

If $\bar{\bar{G}}^E$ does not depend on the distribution density functions $W_B(M)$ and $W_C(M)$, such as in Eq. (6), the treatment leads to relatively simple equations [1, 10, 11]. If $\bar{\bar{G}}^E$ depends on these distribution density functions, stability considerations become more complicated [8, 12]. In the case of Eq. (8), where this dependence is provided by the occurrence of the number-average segment number $\bar{r}_n$, the relation for the spinodal reads

$$0 = \frac{1}{\psi_B \bar{r}_{w,B}} + \frac{1}{(1 - \psi_B)\bar{r}_{w,C}} - 2\beta(T) \frac{\left(1 + \frac{Q}{\bar{r}_n}\right)(1 - \gamma)}{(1 - \gamma\psi_B)^3}$$

$$- 2A \left(\frac{1}{\bar{r}_{w,B}} - \frac{1}{\bar{r}_{w,C}}\right) - A^2 \left[\psi_B \left(\frac{1}{\bar{r}_{n,B}} - \frac{1}{\bar{r}_{w,B}}\right)\right.$$

$$\left. + (1 - \psi_B) \left(\frac{1}{\bar{r}_{n,C}} - \frac{1}{\bar{r}_{w,C}}\right)\right]. \tag{21}$$

At the critical point, the following equation must also be valid:

$$0 = \frac{\bar{r}_{z,B}}{\psi_B^2 \, \bar{r}_{w,B}^2} \, [1 - \psi_B A]^3 - \frac{\bar{r}_{z,C}}{(1 - \psi_B)^2 \, \bar{r}_{w,C}^2} \, [1 + (1 - \psi_B)A]^3$$

$$+ \, 6\beta(T) \left(1 + \frac{Q}{\bar{r}_n}\right) \frac{\gamma(1 - \gamma)}{(1 - \gamma\psi_B)^4} + \frac{6\beta(T)Q(1 - \gamma)}{(1 - \gamma\psi_B)^3} \left(\frac{1}{\bar{r}_{w,B}} - \frac{1}{\bar{r}_{w,C}}\right)$$

$$+ A^2 \left[\frac{A}{\bar{r}_n} - \frac{3}{\bar{r}_{w,B}} + \frac{3}{\bar{r}_{w,C}}\right] + A \left\{\frac{3}{\psi_B \bar{r}_{w,B}} + \frac{3}{\psi_C \bar{r}_{w,C}}\right. \tag{22}$$

$$\left. + \, \frac{6Q\beta(T)(1 - \gamma)}{(1 - \gamma\psi_B)^3} \left[\psi_B \left(\frac{1}{\bar{r}_{n,B}} - \frac{1}{\bar{r}_{w,B}}\right) + (1 - \psi_B) \left(\frac{1}{\bar{r}_{n,C}} - \frac{1}{\bar{r}_{w,C}}\right)\right]\right\}.$$

The parameter

$$A = -\beta(T)Q \, \frac{1 - 2\psi_B + \gamma\psi_B^2}{(1 - \gamma\psi_B)^2} \tag{23}$$

was introduced in these equations. The symbols $\bar{r}_{w,B}$, $\bar{r}_{z,B}$, and the corresponding C quantities are the weight-average and the z- average, respectively.

MODEL CALCULATIONS

The aim of these calculations is to show how the Gibbs free energy relation, Eq. (8), permits the description of the features arising for transitions from polymer mixtures to oligomer mixtures. In the model calculations, the following values were applied: $\bar{r}_{n,B} = 31.12F$; $k_B = 3.46$; $\bar{r}_{n,C} = 26.36F$; $k_C = 1.80$; $\gamma = -0.478$; $Q = -17.40$. To avoid the use of a specific relation for $\beta(T)$, instead of T, the quantity $1/\beta(T)$ was considered; this proved to be roughly proportional to T.

The transition from polymer mixtures to oligomer mixtures was provided by reducing $\bar{r}_{n,B}$ and $\bar{r}_{n,C}$ by a common factor F (Fig. 1). For $F = 1$ the cloud-point curve and the shadow curve show the well-known shape from polymer mixtures (Fig. 1a).

With decreasing F, special features arise with the occurrence of a heterogeneous double plait point (in the terminology by Korteweg [13]) on the spinodal at $\psi_B = 0.63$ and $1/\beta(T) = 4.09$. This heterogeneous double plait

point corresponds to the coincidence of a metastable and an unstable critical point, which separate from each other on further decreasing F. Figure 1(b) shows the cloud-point curve and spinodal close after the occurrence of the heterogeneous double plait point: The two new critical points ($\psi_B^{unstable} <$ $\psi_B^{metastable}$) are still close together. On further decrease of the factor F, the distance between the two new critical points on the spinodal increases, and, furthermore, the metastable critical point approaches the cloud-point curve. In Fig. 1(c), corresponding to $F = 0.666$, this point is already situated beyond this curve, i.e., the metastable critical point has become a stable one. And the attached cloud-point curve is also partially situated in the stable range. It intersects the original cloud-point curve at the triple point describing the coexistence of three different phases. This triple point divides the original and the new cloud-point curves into stable and metastable parts. (Of course, a cloud-point curve attached to the unstable critical point may also be calculated, but it is situated in the unstable range and, hence, is not of practical interest.)

EXAMPLE

As an example, a polystyrene + poly(methylphenylsiloxane) mixture investigated by Nose and coworkers [14] will be considered. Both polydisperse components can be characterized by Schulz-Flory distributions and the parameters are for polystyrene $\overline{M}_n = 8490$ g/mol, $k = 16.7$ and for poly-(methylphenylsiloxane) $\overline{M}_n = 1780$, $k = 1.75$. Hence, at least the poly-(methylphenylsiloxane) is an oligomer.

As pointed out earlier [7], no consistent description of the experimental cloud-point data and the experimental critical point could be obtained when a $\overline{\overline{G}}^E$ relation was applied replacing Huggins χ parameter by a linear function of ψ_B (i.e., Eq. 6 with $d = 0$). This result was in contrast to the calculations for some polystyrene + poly(vinyl methyl ether) systems containing real polymers.

Hence, the more refined $\overline{\overline{G}}^E$ relations, Eqs. (6) and (8), were applied to obtain a good fit to the experimental cloud points as well as to the experimental critical point. In both cases, B means polystyrene, and $\beta(T)$ was assumed to follow
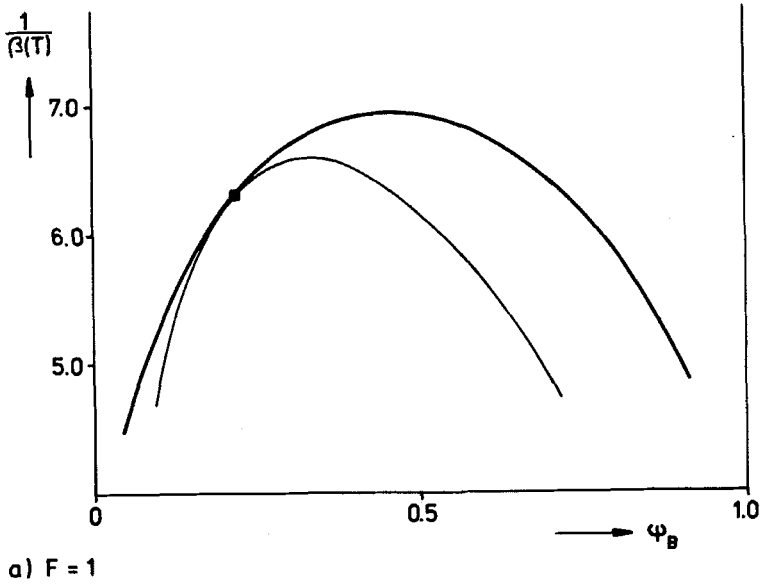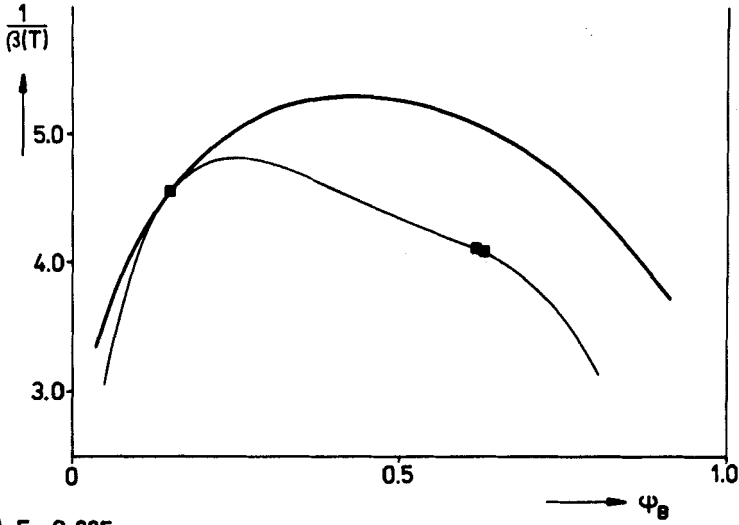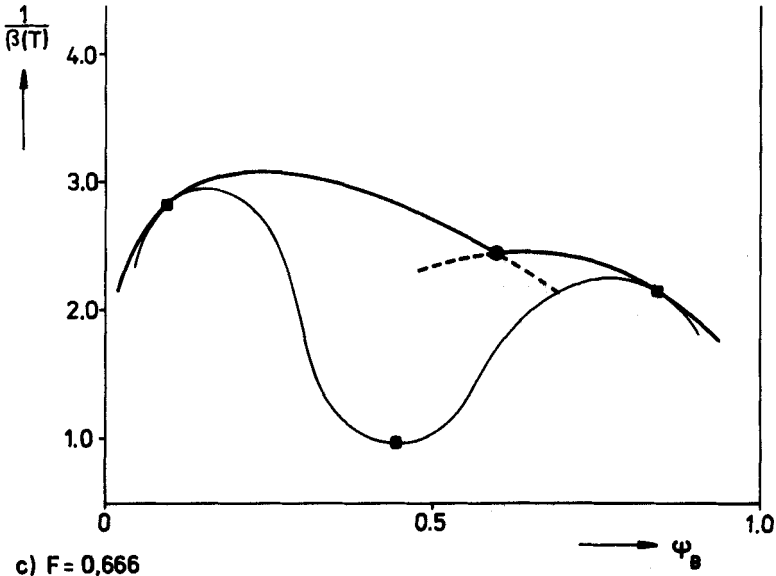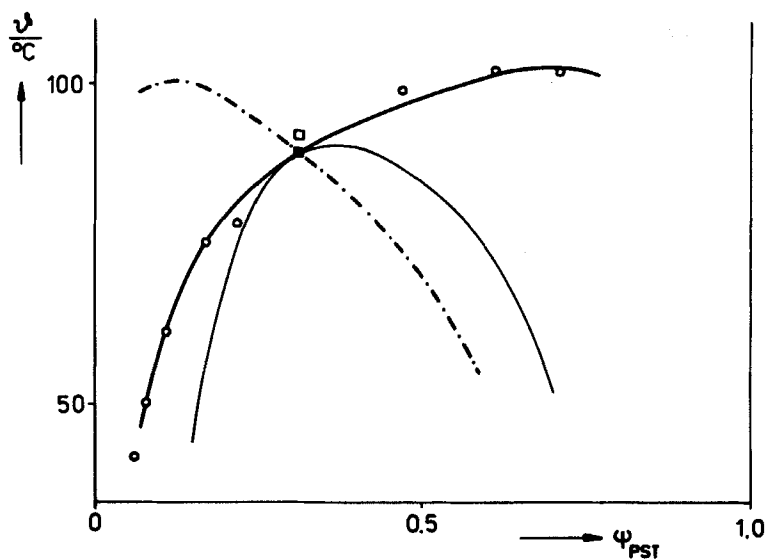
$$\beta(T) = a + b/T. \tag{24}$$

a) F = 1

FIG. 1. Results of model calculations. Cloud-point curves: stable (heavy
lines); metastable (dashed lines); spinodal (light lines). Critical point (■);
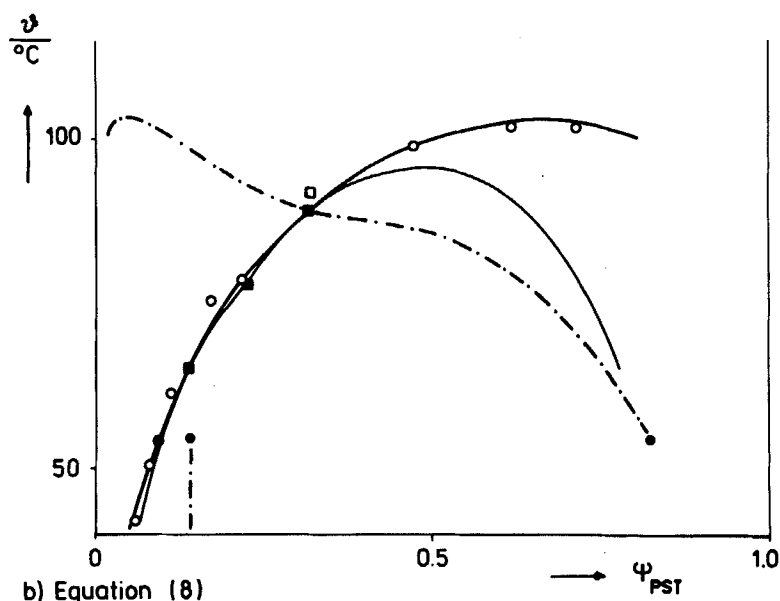triple point (●).

b) F = 0,885

c) F = 0,666

a) Equation (6)

b) Equation (8)

FIG. 2. A polystyrene + poly(methylphenylsiloxane) blend. Experimental data: cloud points (○) and critical point (□). Calculations by means of a model equation. Heavy lines, cloud-point curves; dot-dashed lines, shadow curves; light lines, spinodal. Critical points (■); triple points (●).

For Eq. (6), the fit led to $a = -0.00020\, M_S/(g/mol)$, $b/K = 0.2557\, M_S/(g/mol)$, $c = -0.164$, $d = 0.4094$; and for Eq. (8) to $a = -0.00114\, M_S/(g/mol)$, $b/K = 0.4957\, M_S/(g/mol)$, $\gamma = -0.775$, $Q = -13.89$, where M_S is the molecular weight of a segment which was considered to be approximately equal for both polydisperse components. For the calculations, $M_S = 100$ g/mol was used. The result of the fits and the calculated shadow curves and spinodals are shown in Fig. 2. It can be seen that a good fit to the experimental cloud points and the experimental critical point is achieved in both cases. Equation (6) has the disadvantage of lacking dependence on averages of the MWD. If such a dependence is introduced, it usually results in a further increase in the number of parameters. Equation (8) contains only four parameters, like Eq. (6), but depends on the number-average segment number. For the case of this equation, some special features are predicted: the occurrence of two stable critical points situated on the same cloud-point curve and of an unstable critical point between them. Furthermore, the occurrence of a triple point, i.e., of a three-phase equilibrium, at lower temperatures is predicted. Whether these predictions correspond to the true behavior cannot be said without knowledge of further experimental details.

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