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ON THE PRECIPITATION THRESHOLD OF SOLUTIONS OF HETEROGENEOUS POLYMERS IN FLORY–HUGGINS SYSTEMS WITH A CONCENTRATION-DEPENDENT PAIR-INTERACTION PARAMETER

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Abstract—Equations are derived for $(dT/d\phi)_p$ and $(dp/d\phi)_T$ along the cloud-point curves of solutions of heterogeneous polymers in a single solvent. It is shown that the extreme of the cloud-point curve (the precipitation threshold) can be calculated using these equations. The results of some model calculations on systems obeying the Flory–Huggins equation with a pair-interaction parameter of the form $g(\phi, T, p) = g_0(T, p) + g_1\phi + g_2\phi^2$ are given, revealing the influence of g_1 and g_2 on the precipitation threshold.

INTRODUCTION

Solutions of heterogeneous polymers are systems of more than two components. If demixing occurs in such systems, the extremes of the cloud-point curves (plots of precipitation temperature against solute concentration at constant pressure or precipitation pressure against solute concentration at constant temperature) are not in general critical points as has been pointed out by Tompa [1]. This is easily seen in Figs. 1 and 2. Figure 1 illustrates the case of a three component liquid system consisting of a solvent O and two homologous linear polymer components P_1 and P_2 of different chain lengths at constant pressure. Several binodials at constant temperature are shown. In this system the miscibility increases with increasing temperature T. The line OP represents all systems containing the given polymer P (a mixture of P_1 and P_2) and the solvent O. The construction of the quasi-binary section TOP yields the cloud-point curve (hereafter designated as CPC) Fig. 2. It is clear that the critical point (ϕ_C, T_5) does not coincide with the extreme of the CPC (ϕ_{th}, T_3). Tompa called the latter point the precipitation threshold which, in this case, represents the highest temperature at which phase separation can occur. The relationships are entirely analogous for a system consisting of N polymer species and a solvent. The composition of the system can be represented in a N-dimensional tetrahedron. The binodial curve is replaced by a $(N$-$1)$ dimensional binodial surface. The given polymer P is represented

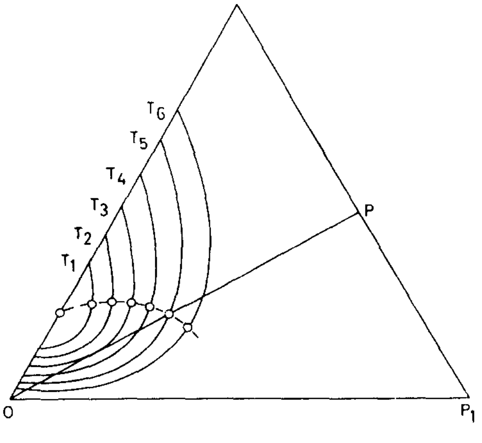

Fig. 1. Binodials of a ternary liquid system with a two-phase region at constant temperature and pressure. Binodials at several temperatures are shown. The critical points are denoted by circles.

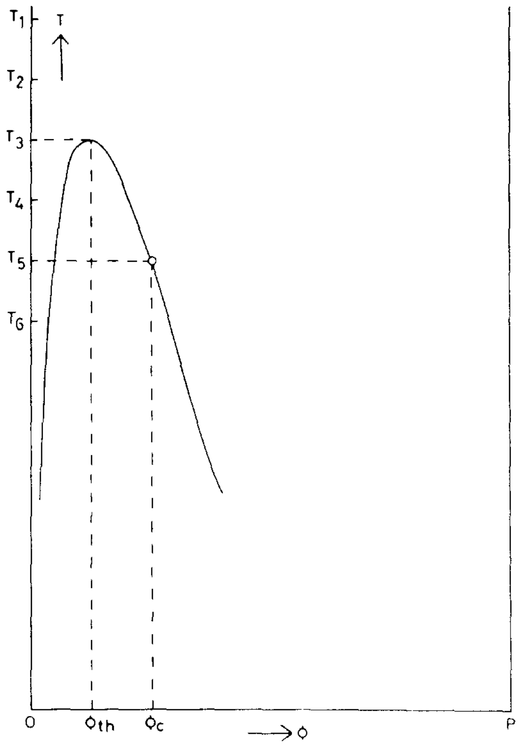

Fig. 2. The cloud point curve: a quasi-binary section of Fig. 1.

by a point P in the $(N\text{-}1)$ dimensional face of the tetrahedron opposite to the solvent corner O. The CPC can be found as the quasi-binary section TOP and shows the same features as Fig. 2. In general the precipitation threshold is determined by the binodial surface to which the composition axis OP is a tangent.

In this paper equations for $\mathrm{d}T/\mathrm{d}\phi$ and $\mathrm{d}p/\mathrm{d}\phi$ along the CPC are derived. Using the Flory–Huggins equation with a concentration dependent pair-interaction parameter for the free enthalpy of mixing, and putting $\mathrm{d}T/\mathrm{d}\phi = 0$ $\mathrm{d}p/\mathrm{d}\phi = 0$, we find the conditions for the precipitation threshold.

THEORY

The Flory–Huggins expression for the free enthalpy of mixing $\Delta\overline{G}$ of a mixture of N homologous polymer components in a single solvent reads [2]:

$$\Delta\overline{G}/RT = \phi_0 \ln \phi_0 + \sum_{i=1}^{N} \phi_i m_i^{-1} \ln \phi_i + g\phi\phi_0 \qquad (1)$$

ϕ_0 $(i = 0)$ and ϕ_i are the composition variables for the solvent and polymer component i respectively and can be expressed as volume-fractions, weight-fractions or segment mol-fractions. m_i is the size of a molecule of polymer component i relative to the size of the solvent molecule $(m_0 = 1)$.

$$\phi = \sum_{i=1}^{N} \phi_i$$

is the overall polymer concentration and g is the pair-interaction parameter. $\Delta\overline{G}$ must be taken per unit of volume, unit of weight or per mol segments, depending on the definition of the composition variables.

In the original treatments by Flory and Huggins, g was considered as a function of temperature only. This soon appeared to be an oversimplification. The experimental data show that g often depends on ϕ as well on the molecular weight of the polymer.

The concentration of polymer component i in a homogeneous solution ϕ_i and in the solvent-free liquid polymer ϕ_i^0 are related by the equation for the composition axis OP (Fig. 1):

$$\phi_i = \phi_i^0 \phi \qquad (2)$$

ϕ_i^0 is determined by the molecular-weight distribution of the polymer. The equilibrium conditions for a system of $(N + 1)$ components separated in two phases (′ and ″) are:

$$\mu_i' = \mu_i'' \qquad (i = 0, 1, 2, \ldots, N) \qquad (3)$$

where μ_i is the chemical potential.
For both phases we have the Gibbs–Duhem equation:

$$\overline{V}'\,\mathrm{d}p - \overline{S}'\,\mathrm{d}T = \sum_{i=0}^{N} \phi_i'\,\mathrm{d}\mu_i' \qquad (4a)$$

$$\overline{V}''\,\mathrm{d}p - \overline{S}''\,\mathrm{d}T = \sum_{i=0}^{N} \phi_i''\,\mathrm{d}\mu_i''. \qquad (b)$$

If pressure, temperature and compositions of the two phases are changed by small amounts $\mathrm{d}p$, $\mathrm{d}T$, $\mathrm{d}\phi_i'$ and $\mathrm{d}\phi_i''$ in such a way that the two phases remain in equilibrium we have $\mathrm{d}\mu_i' = \mathrm{d}\mu_i'' = \mathrm{d}\mu_i$. Substraction of Eqns. (4a) and (4b) gives then:

$$(\overline{V}' - \overline{V}'')\mathrm{d}p - (\overline{S}' - \overline{S}'')\mathrm{d}T = \sum_{i=0}^{N} (\phi_i' - \phi_i'')\mathrm{d}\mu_i. \qquad (5)$$

It may easily be shown (see for instance Haase[3] or Malesinski[4]) that, if μ_i is considered as a function of $T, p, \phi_1', \phi_2', \ldots, \phi_N'$, Eqn. (5) can be worked out in:

$$\sum_{i=1}^{N} \phi_i''\Delta v_i\,\mathrm{d}p - \sum_{i=1}^{N} \phi_i''\Delta s_i\,\mathrm{d}T = \sum_{i=1}^{N}\sum_{j=1}^{N} (\phi_i' - \phi_i'') \times \left(\frac{\partial^2 \overline{G}'}{\partial\phi_i'\partial\phi_j'}\right)_{T,p} \mathrm{d}\phi_j' \qquad (6)$$

where $\Delta v_i = v_i' - v_i''$ and $\Delta s_i = s_i' - s_i''$. v_i and s_i are the partial derivatives of the volume and the entropy with respect to the "amount" of component i. The way in which this "amount" is defined depends on the chosen definition of the composition variables. The CPC is the borderline between the one-phase area and the two-phase area.

This means that each point of the CPC lies on the composition axis OP. So if we denote the principal phase by ′ and the conjugate (i.e. appearing) phase by ″. we have along the CPC [Eqn. (2)]:

$$\phi_j' = \phi_j^0 \phi' \qquad (7)$$

and since ϕ_j^0 is constant:

$$\mathrm{d}\phi_j' = \phi_j^0\,\mathrm{d}\phi' \qquad (8)$$

From Eqn. (1) it follows that:

$$\frac{1}{RT}\left(\frac{\partial^2 \overline{G}}{\partial\phi_i\partial\phi_j}\right)_{T,p} = \phi_0^{-1} - 2g + 2(1 - 2\phi)\frac{\partial g}{\partial\phi} + \phi_0\phi\frac{\partial^2 g}{\partial\phi^2} = L \quad \text{if} \quad i \neq j \qquad (9a)$$

and

$$\frac{1}{RT}\left(\frac{\partial^2 \overline{G}}{\partial\phi_i\partial\phi_j}\right)_{T,p} = L + (m_i\phi_i)^{-1} \qquad \text{if} \quad i = j. \qquad (b)$$

Equations (6) and (8) together with Eqn. (9) give:

$$-\sum_{i=1}^{N} \phi_i''\Delta s_i\,\mathrm{d}T + \sum_{i=1}^{N} \phi_i''\Delta v_i\,\mathrm{d}p = RT\left[(\phi_0'' - \phi_0')L' + (\phi')^{-1}\cdot\sum_{i=1}^{N}\frac{\phi_i' - \phi_i''}{m_i}\right]\mathrm{d}\phi'. \qquad (10)$$

From Eqn. (10) we find $(\mathrm{d}T/\mathrm{d}\phi)_p$ or $(\mathrm{d}p/\mathrm{d}\phi)_T$ along the CPC in a quasi-binary temperature-composition section or a quasi-binary pressure-composition section respectively. The precipitation threshold is defined by $(\mathrm{d}T/\mathrm{d}\phi)_p = 0$ or $(\mathrm{d}p/\mathrm{d}\phi)_T = 0$ which yields:

$$(\phi_0'' - \phi_0')L'\phi' + \sum_{i=1}^{N}\frac{\phi_i' - \phi_i''}{m_i} = 0. \qquad (11)$$

Equation (11) reduces to the equation which was derived, in a different way, by Tompa for a concentration-independent g [1].

CALCULATION PROCEDURES

The precipitation threshold can in principle be calculated from Eqns. (11) and (7) together with Eqn. (3) for the solvent:

$$\ln(1-\phi') + \sum_{i=1}^{N} \frac{m_i - 1}{m_i}\phi_i' + [g' - (1-\phi')\delta']\phi'^2$$

$$= \ln(1-\phi'') + \sum_{i=1}^{N} \frac{m_i - 1}{m_i}\phi_i''$$

$$+ [g'' - (1-\phi'')\delta'']\phi''^2 \qquad (12)$$

and the well-known equation for the distribution coefficient of polymer species i over the two phases[2]:

$$\phi_i''/\phi_i' = \exp(\sigma m_i) \qquad (13a)$$

with

$$\sigma = \ln[(1-\phi'')/(1-\phi')] - (g'' - g')$$

$$+ 2(g''\phi'' - g'\phi') - [(1-\phi'')\phi''\delta'' - (1-\phi')\phi'\delta'] \qquad (b)$$

where $g' = g(\phi')$; $g'' = g(\phi'')$; $\delta' = (\partial g/\partial\phi)_{\phi'}$; $\delta'' = (\partial g/\partial\phi)_{\phi''}$. With these equations and a given set of values of m_i and ϕ_i^0, i.e. the molecular-weight distribution of the polymer, one can calculate the precipitation threshold in terms of concentration and temperature at a given pressure or concentration and pressure at a given temperature if g is known as a function of temperature, pressure and concentration. Huggins [5] suggested to approximate the concentration dependence of g by a polynomial in ϕ. This concept, also followed by Koningsveld [6], leads to the following expression for g:

$$g = \sum_{k}^{n} g_k\phi^k \qquad k = 0, 1, 2, \ldots, n, \qquad (14)$$

In this formula each coefficient g_k may be a function of temperature and pressure. If we restrict ourself to a quadratic dependence of g on ϕ and suppose that g_1 and g_2 are independent of temperature and pressure equations, (7), (11), (12) and (13) can be worked out in:

$$g_1 = \{-\sigma + I_1[1 - (\phi'' - \phi')/2] - \tfrac{1}{2}(\phi'' - \phi')^2$$

$$\times (1-\phi')^{-1} - 3g_2[\phi'(2\phi' - 1)[2(\phi'' - \phi')$$

$$- (\phi''^2 - \phi'^2)] + (\phi''^2 - \phi'^2) - 2(\phi''^3 - \phi'^3)$$

$$+ (\phi''^4 - \phi'^4)]\}/\{3\phi'[2(\phi'' - \phi')$$

$$- (\phi''^2 - \phi'^2)] - 3(\phi''^2 - \phi'^2) + 2(\phi''^3 - \phi'^3)\} \qquad (15)$$

$$g_0 = \tfrac{1}{2}I_1(\phi'' - \phi')^{-1} - 3\phi'[g_1 - g_2(1 - 2\phi')]$$

$$+ g_1 + \tfrac{1}{2}(1-\phi')^{-1} \qquad (16)$$

$$\phi'' = \phi' I_2 \qquad (17)$$

where

$$I_1 = \sum_{i=1}^{N} \phi_i^0 m_i^{-1}[\exp(\sigma m_i) - 1] \qquad (18)$$

$$I_2 = \sum_{i=1}^{N} \phi_i^0 \exp(\sigma m_i). \qquad (19)$$

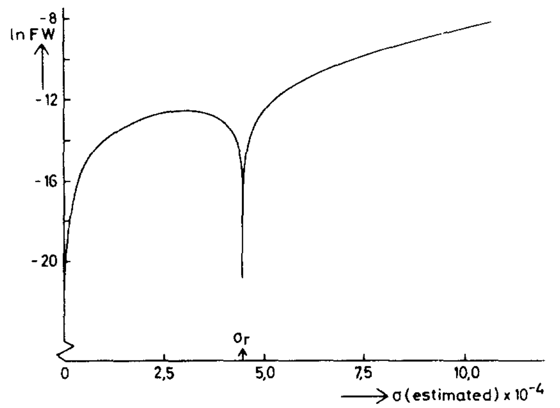

Fig. 3. The optimalization method.

$$\mathrm{FW} = \left|\frac{\sigma(\text{calculated}) - \sigma(\text{estimated})}{\sigma(\text{estimated})}\right|.$$

The physical significant root σ_r is found at $\sigma = 4{,}495 \cdot 10^{-4}$.

For a given molecular-weight distribution and known $g_0(p, T)$, g_1 and g_2 the precipitation threshold can be calculated as follows:

(a) Introduce estimated values of ϕ' and σ and calculate I_1, I_2, ϕ'', g_1 and g_0 from Eqns. (18), (19), (17), (15) and (16) respectively.

(b) Calculate σ (calculated) from Eqn. (13b).

(c) With the aid of a suitable optimalization method σ (estimated) is changed at constant ϕ' and g_2 until

$$\left|\frac{\sigma(\text{calculated}) - \sigma(\text{estimated})}{\sigma(\text{estimated})}\right| < 10^{-8}.$$

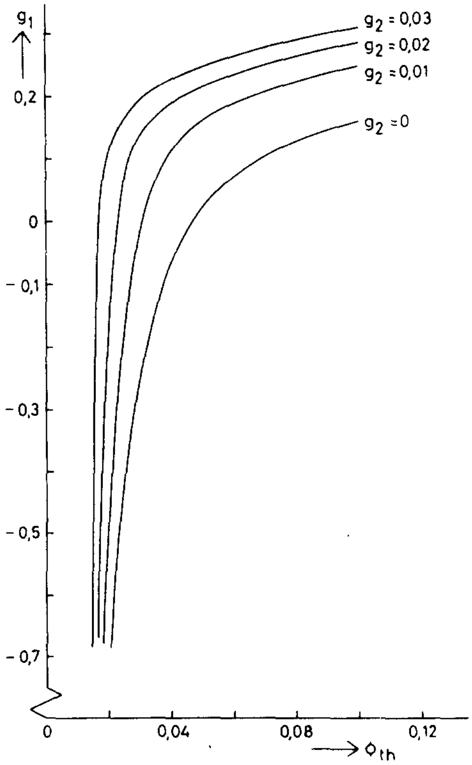

Fig. 4. The precipitation threshold. g_1 as a function of ϕ_{th} at constant g$_2$. $m_n = 50$, $m_w = 100$, $m_z = 150$.

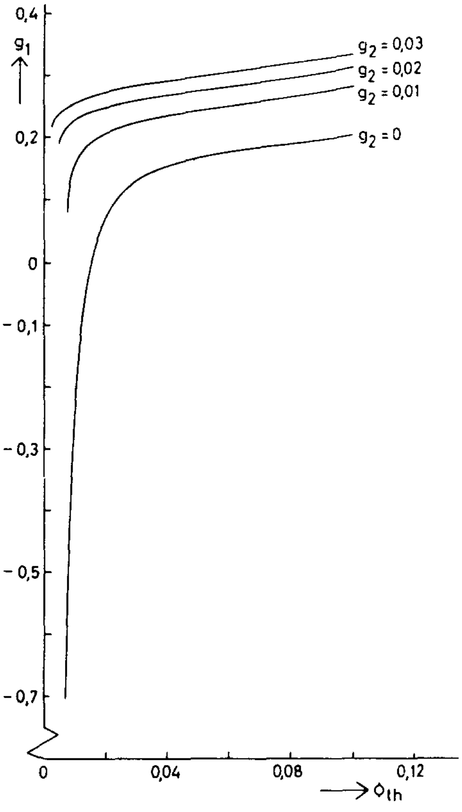

Fig. 5. The precipitation threshold. g_1 as a function of ϕ_{th} at constant g_2. $m_n = 500$, $m_w = 1000$, $m_z = 1500$.

(d) Repeat the calculation with various values of ϕ'. From a plot of g_1 vs ϕ' one can find the precipitation threshold (g_0, ϕ') at the desired g_1-value. From $g_0(p, T)$ at a given p or at a given T we can calculate the temperature or pressure of the precipitation threshold respectively.

For the optimalization method we used the Marquardt method [7]. A typical plot of

$$\ln \left| \frac{\sigma(\text{calculated}) - \sigma(\text{estimated})}{\sigma(\text{estimated})} \right| \text{ vs } \sigma(\text{estimated})$$

at constant ϕ' and g_2 is shown in Fig. 3. The physically significant root is found at $\sigma = 4.495 \times 10^{-4}$. The plot shows that Tompa's remark (that calculations of this kind require a very high accuracy for σ if significant results are to be obtained) is highly relevant [1]. The calculation of one point of a g_1-ϕ' plot requires about 1.5 sec computer time on an IBM 370/165 system.

SOME MODEL CALCULATIONS

Many studies of thermodynamic properties of polymer solutions have shown that the pair-interaction parameter generally depends on the polymer concentration. It seems therefore worthwhile to check the influence of g_1 and g_2 on the location of the precipitation threshold. We will leave the temperature and pressure dependence of g_0 unspecified. Figures 4 and 5 show the influence of g_1 and g_2 on the precipitation threshold for two exponential molecular-weight distribution functions [8] w_1 and w_2.

For w_1: $m_n = 50$; $m_w = 100$; $m_z = 150$. For w_2: $m_n = 500$; $m_w = 1000$; $m_z = 1500$.

The various averages of the relative chain length are defined by:

$$m_n = 1/\Sigma\, \phi_i^0/m_i \tag{20}$$

$$m_w = \Sigma\, \phi_i^0 m_i \tag{21}$$

$$m_z = \Sigma\, \phi_i^0 m_i^2/\Sigma\, \phi_i^0 m_i. \tag{22}$$

From these figures it can be seen that at constant g_2 an increase in g_1 shifts the precipitation threshold towards higher polymer concentrations. This is in accordance with the findings of Koningsveld *et al.* [9] who studied the influence of g_1 at $g_2 = 0$ on the whole CPC. An increase of g_2 at constant g_1 is accompanied with a shift of the precipitation threshold towards lower polymer concentrations.

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