



Modeling of the (liquid + liquid) equilibrium of polydisperse hyperbranched polymer solutions by lattice-cluster theory



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ABSTRACT

The (liquid + liquid) equilibrium of solutions of hyperbranched polymers of the Boltorn type is modeled in the framework of lattice-cluster theory. The association effects are described by the chemical association models CALM (for self association) and ECALM (for cross association). For the first time the molar mass polydispersity of the hyperbranched polymers is taken into account. For this purpose continuous thermodynamics is applied. Because the segment-molar excess Gibbs free energy depends on the number average of the segment number of the polymer the treatment is more general than in previous papers on continuous thermodynamics. The polydispersity is described by a generalized Schulz–Flory distribution. The calculation of the cloud-point curve reduces to two equations that have to be numerically solved. Conditions for the calculation of the spinodal curve and of the critical point are derived. The calculated results are compared to experimental data taken from the literature. For Boltorn solutions in non-polar solvents the polydispersity influence is small. In all other of the considered cases polydispersity influences the (liquid + liquid) equilibrium considerably. However, association and polydispersity influence phase equilibrium in a complex manner. Taking polydispersity into account the accuracy of the calculations is improved, especially, in the diluted region.

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1. Introduction

Recently, the importance of hyperbranched polymers (HBPs) has continuously increased. These polymers with a tree-like structure can be easily synthesized via one-step reactions. The branching influences considerably the thermodynamic properties. In comparison with linear polymers HBPs show a reduced viscosity in solutions and in melts and a high solubility in common solvents. Their properties may be tailored by modification of the numerous end groups. There are many possible applications for these materials [1–10].

Most HBPs possess a large number of terminal hydroxyl groups. To calculate the (liquid + liquid) equilibrium (LLE) of HBP solutions one has to describe simultaneously the branching influence, the association effects and the polydispersity influence. A suitable branching treatment is given by the lattice-cluster theory (LCT), developed by Freed and co-workers [11–16]. In last years LCT has been successfully applied to the calculation of the LLE of HBP solutions [17–28]. In this, the original voluminous equations of the LCT were step by step simplified. Now, the architecture of a

molecule may be described by three geometrical parameters only. Furthermore, association terms were included [19–25]. Either these terms were based on Wertheim's theory [19,21–24] or on chemical association models [20,25]. Therefore, branching and association in HBP solutions may be adequately described. However, polydispersity effects were generally neglected. On the one hand, this originates from the lack of experimental information. On the other hand, a suitable theoretical treatment had to be developed. In this paper we take the molar mass polydispersity into account. Žagar *et al.* [29] studied experimentally HBPs of the Boltorn type including also values of the number average and of the weight average of molar mass. So, the most important characterization parameters of molar mass polydispersity are approximately known. Introducing some approximations that are suitable to polymer solutions our equations are simplified in a way permitting an extension to the polydisperse case. In this, the association effects are described by the chemical association models CALM in the case of self association [20,30] and ECALM [20,25,31], if also cross association occurs. The theoretical treatment of polydispersity is based on continuous thermodynamics [32–35]. Because the segment-molar excess Gibbs free energy depends on the number average of the segment number the treatment is somewhat more complicated than in previous papers

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dealing with continuous thermodynamics. We derive equations for the calculation of the cloud-point curve, of the spinodal curve and of the critical point. For several solutions of Boltorn polymers the cloud-point curve and the critical point are calculated and compared to the experimental data. We will show that the consideration of polydispersity improves the accuracy of the description. Especially, the relatively high experimental cloud-point temperatures for diluted Boltorn solutions may be explained by the molar mass polydispersity of the polymers.

2. Theory

2.1. Lattice-cluster theory and chemical association theories

In the framework of continuous thermodynamics [32–35] the segment-molar Gibbs free energy ΔG_s (without the pure component contributions) reads

$$\frac{\Delta G_s}{RT} = \frac{\phi_A}{r_A} \ln \phi_A + \int_0^\infty \frac{1}{r_B} \phi_B W_B(r_B) \ln[\phi_B W_B(r_B)] dr_B + \frac{G_s^E}{RT};$$

$$\phi_A = 1 - \phi_B. \quad (1)$$

The first two terms of equation (1) represent the well-known athermal Flory–Huggins contribution. T is the temperature and R is the universal gas constant. G_s^E is the segment-molar excess Gibbs free energy describing the intermolecular interactions. ϕ_A is the segment fraction of the solvent and ϕ_B is the total segment fraction of the polymer. r_A, r_B are the segment numbers of the solvent molecules and of the polymer species. $W_B(r_B)$ is the segment-molar distribution function of the polymer. It is the continuous analogy to the segment fraction of a certain polymer species if there is no solvent but many other polymer species. The general moment $\bar{r}_B^{(\alpha)}$ of the distribution function is defined as

$$\bar{r}_B^{(\alpha)} = \int_0^\infty (r_B)^\alpha W_B(r_B) dr_B; \quad \alpha = -1, 0, 1, 2, 3, \dots \quad (2)$$

There are two important special moments. The first of them corresponds to the normalization condition of the distribution function expressed by $\bar{r}_B^{(0)} = 1$. Furthermore, the number average of the segment number \bar{r}_B is given by $\bar{r}_B = 1/\bar{r}_B^{(-1)}$. The most of the previous papers [32–35] on continuous thermodynamics assume G_s^E to be only a function of ϕ_B and T . However, the segment-molar excess Gibbs free energy can be a functional of $W_B(r_B)$ meaning G_s^E can be dependent on moments of the distribution function. In this paper we will show that based on the lattice-cluster theory (LCT) and on the applied association models G_s^E depends on \bar{r}_B in the following way

$$\frac{G_s^E}{RT} = A + B \frac{\phi_B}{\bar{r}_B}, \quad (3)$$

where the quantities A and B are functions of ϕ_B and T . In this paper we calculate A and B generally on the base of the lattice-cluster theory including association effects. Here, we distinguish between the following four cases: Disregarding of association effects (section 2.1.1), consideration of self association for solutions of HBPs in non-polar solvents (section 2.1.2), assumption of cross associates and self associates of the solvent molecules (section 2.1.3), assumption of cross associates and self associates of the polymer molecules (section 2.1.4).

2.1.1. Disregarding of association effects

Here, only the LCT is applied. Freed *et al.* [11–16] introduced the LCT taking the architecture of the molecules into account. They expanded the Helmholtz free energy in a double power series of $1/z$ and $\varepsilon/(k_B T)$. The quantity z is the coordination number of the

lattice, k_B is the Boltzmann constant and ε is defined by $\varepsilon = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB}$.

$\varepsilon_{AA}, \varepsilon_{BB}$ and ε_{AB} characterize the interaction energies of contact pairs of the type AA, BB and AB. The quantity $\varepsilon/(k_B T)$ relates to the usual χ -parameter of the Flory–Huggins theory by $\chi = z\varepsilon/(2k_B T)$. The series expansion is truncated after the second order terms in $1/z$ and in $\varepsilon/(k_B T)$. The treatment assumes an incompressible lattice and results for a binary system in [17–27]

$$\frac{G_s^E}{RT} = \sum_{i=1}^{i=6} \alpha_i \phi_B^i. \quad (4)$$

The sum with the quantities α_i ($i = 1, 2, \dots, 6$) takes the architecture of the molecules into account (the equations for α_i are listed in appendix A). Originally, the architecture of the B-molecules was described by the six geometric parameters K_1, K_2, \dots, K_6 and that of the A-molecules by L_1, L_2, \dots, L_6 [7–14]. However the geometric parameters are connected by the relations [5,10,15–17]

$$K_1 + 2K_2 + 2K_5 - K_1^2 r_B = 0, \quad (5a)$$

$$2K_2 + 2K_3 + 3K_4 + K_6 - K_1 K_2 r_B = 0 \quad (5b)$$

and

$$L_1 + 2L_2 + 2L_5 - L_1^2 r_A = 0, \quad (6a)$$

$$2L_2 + 2L_3 + 3L_4 + L_6 - L_1 L_2 r_A = 0. \quad (6b)$$

Because of these equations the quantities α_i (appendix A) contain only the geometrical parameters K_1, K_2, K_3 and L_1, L_2, L_3 . Furthermore, the segment numbers r_A and r_B do not occur in α_i explicitly. The parameters K_1, K_2, K_3 and L_1, L_2, L_3 are defined by

$$K_1 = N_{1,B}/r_B; \quad K_2 = N_{2,B}/r_B; \quad K_3 = N_{3,B}/r_B, \quad (7a)$$

$$L_1 = N_{1,A}/r_A; \quad L_2 = N_{2,A}/r_A; \quad L_3 = N_{3,A}/r_A. \quad (7b)$$

For a chain of segments of the type $i = A, B$ the quantity $N_{1,i}$ is the number of bonds, $N_{2,i}$ is the number of two consecutive bonds and $N_{3,i}$ is the number of three consecutive bonds. In the case of the small solvent molecules A these numbers may be easily counted. To calculate them for the polymer molecules one needs only the segment number r_B and the numbers $b_{3,B}$ and $b_{4,B}$ of branching points of degrees 3 and 4 (points in which 3 or 4 chains meet together). There are the following relations [5]

$$K_1 = (r_B - 1)/r_B, \quad (8a)$$

$$K_2 = (r_B - 2 + b_{3,B} + 3b_{4,B})/r_B, \quad (8b)$$

$$K_3 = (r_B - 3 + 2b_{3,B} + 6b_{4,B})/r_B. \quad (8c)$$

Equation (8a) is valid without any restriction. Equation (8b) may be applied for all molecules with two or more segments. Equation (8c) requires that all branches of the chain contain at least two bonds. For most HBPs this condition is fulfilled. If the segment number of the HBP is sufficiently high equations (8a)–(8c) may be replaced in very good approximation by

$$K_1 = 1, \quad (9a)$$

$$K_2 = 1 + \tilde{b}_3 + 3\tilde{b}_4, \quad (9b)$$

$$K_3 = 1 + 2\tilde{b}_3 + 6\tilde{b}_4. \quad (9c)$$

Here, $\tilde{b}_3 = b_{3,B}/r_B$ and $\tilde{b}_4 = b_{4,B}/r_B$ may be approximately considered to be independent of the segment number r_B . For instance, in the case of the Boltorn polymers H20, H30, H40 one can show $\tilde{b}_3 \approx 1/4$ and $\tilde{b}_4 \approx 0$ [7]. The LCT is derived for hypercubic lattices in d dimensions for which $z = 2d$. For the interesting case $d = 3$ the

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