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Note of the estimation of the Θ temperature and ψ parameter from the critical temperature data

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Summary

Critical values of the polymer volume fraction $\varphi_{2,c}$ and the interaction parameter χ_c have been computed for the case that the equation for the chemical potential of solvent contains terms $\nu_c\varphi_2^3$ and $\zeta_c\varphi_2^4$ in addition to $\chi\varphi_2^2$. For $0 \leq \nu_c \leq 1/3$, the limits for infinite chain length are $\varphi_{2,c}^{\infty} = 0$ and $\chi_c^{\infty} = 0.5$. Quite different results are obtained for $\nu_c > 1/3$, $\varphi_{2,c}^{\infty}$ being finite and χ_c^{∞} lower than 1/2. Conclusions for the estimation of the Θ temperature and the entropy-of-dilution ψ parameter are discussed.

Introduction

In the classic theory of phase equilibria in polymer solutions advanced by Shultz and Flory [1,2], the chemical potential of the solvent $\Delta\mu_1$ is expressed by the equation

$$\Delta\mu_1/RT = \ln\varphi_1 + (1 - 1/m)\varphi_2 + \chi\varphi_2^2 \tag{1}$$

where m is the number of segments per chain, χ is the polymer-solvent interaction parameter, φ_1 and φ_2 are, respectively, the volume fractions of the solvent and polymer. The theory leads to simple dependences on m of the critical values of φ_2 and χ,

$$\varphi_{2,c} = (1 + m^{1/2})^{-1} \tag{2}$$

$$\chi_c = (1/2)(1 + m^{-1/2})^2 \tag{3}$$

or

$$\chi_c = (1/2) + (m^{-1/2} + \frac{1}{2}m^{-1}) \tag{4}$$

The limits for infinite chains are

$$\varphi_{2,c}^{\infty} = 0 \text{ and } \chi_c^{\infty} = 1/2 \tag{5}$$

Assuming χ to be given by the equation

$$\chi = \frac{1}{2} - \psi(1 - \Theta/T) \tag{6}$$

where ψ is the entropy-of dilution parameter and Θ is the Flory theta temperature, the well known result is obtained from eq(3) for the dependence on m of the critical temperature

$$1/T_c = (1/\Theta) + (1/\Theta\psi)(m^{-1/2} + \frac{1}{2}m^{-1}). \tag{7}$$

where

$$\Theta = \lim_{1/m \to 0} T_c$$

For high values of m it simplifies to

$$1/T_c = (1/\Theta) + (1/\Theta\psi)m^{-1/2} \tag{8}$$

Eqs (7) and (8) are currently used to estimate Θ and ψ.

According to the theory of polymer solutions [2], the Flory temperature estimated from phase equilibria, Θ^{PE}, should be equal to the temperature, Θ^{A}, at which the second virial coefficient A_2 vanishes. However, by carefully analyzing data for polystyrene and polyethylene, Kamide et al.[3–5] have found that the Θ^{PE} values (of both the LCST and UCST types, $\Theta_{\mathrm{L}}^{\mathrm{PE}}$ and $\Theta_{\mathrm{U}}^{\mathrm{PE}}$) differ from Θ^{A}, and assigned this finding to χ being dependent on concentration.

Assuming χ to depend on φ_2 is mathematically equivalent to extending eq (1) into eq (9) [6,7]

$$\Delta\mu_1/RT = \ln\varphi_1 + (1 - 1/m)\varphi_2 + \chi\varphi_2^2 + \nu\varphi_2^3 + \zeta\varphi_2^4 + \ldots \tag{9}$$

which comprises three interaction parameters (χ, ν, ζ) that are independent of concentration. Tompa [6], and Huggins and Okamoto [7] have found that inclusion of higher terms into eqn (1) significantly changes the coordinates of the critical point for finite chains, and Flory and Daoust [8] have shown that, for infinite chain length, the critical concentration $\varphi_{2,c}^{\infty}$ need not be zero, in contrast to what is predicted by eq (5).

It seemed worth while examining eqn (9) in more detail fo find conditions where the Θ^{PE} temperature differs from Θ^{A}.

Results and Discussion

Differentiating eqn (9) with respect to φ_1 and equating the result to zero, we obtain

$$(1/RT)(\partial\Delta\mu_1/\partial\varphi_1) \equiv (1/\varphi_1) - (1 - 1/m) - 2\chi\varphi_2 - 3\nu\varphi_2^2 - 4\zeta\varphi_2^3 = \Theta \tag{10}$$

A second derivative gives

$$(1/RT)(\partial^2\Delta\mu_1/\partial\varphi_1^2) = -(1/\varphi_1^2) + 2\chi + 6\nu\varphi_2 + 12\zeta\varphi_2^2 = 0 \tag{11}$$

Equations for $\chi = \chi_c$ and $\varphi_2 = \varphi_{2,c}$ at the critical point for phase separation can be deduced from these equations.

By eliminating χ_c from eqs (10) and (11) we obtain

$$(\varphi_{2,c}/\varphi_{1,c})^2 - 3\nu_c\varphi_{2,c}^2 - 8\zeta_c\varphi_{2,c}^3 = 1/m \tag{12}$$

For fixed values of ν_c and ζ_c (assuming ν and ζ to be independent of temperature) and for varying $\varphi_{2,c}$ we calculate the values of m which satisfy eqn (12) (Fig. 1).

For $\nu_c \leq 1/3$, the left hand side is always positive, irrespectively of ζ_c and $\varphi_{2,c}$. However, with $\nu_c > 1/3$, physically meaningful, positive values of m are obtained only if $\varphi_{2,c}$ is larger than a certain value, $\varphi_{2,c}^{*}$, (which depends on ν_c and ζ_c). That means that, in this case, the critical concentration $\varphi_{2,c}^{\infty}$ for infinite chains is not equal to zero as predicted

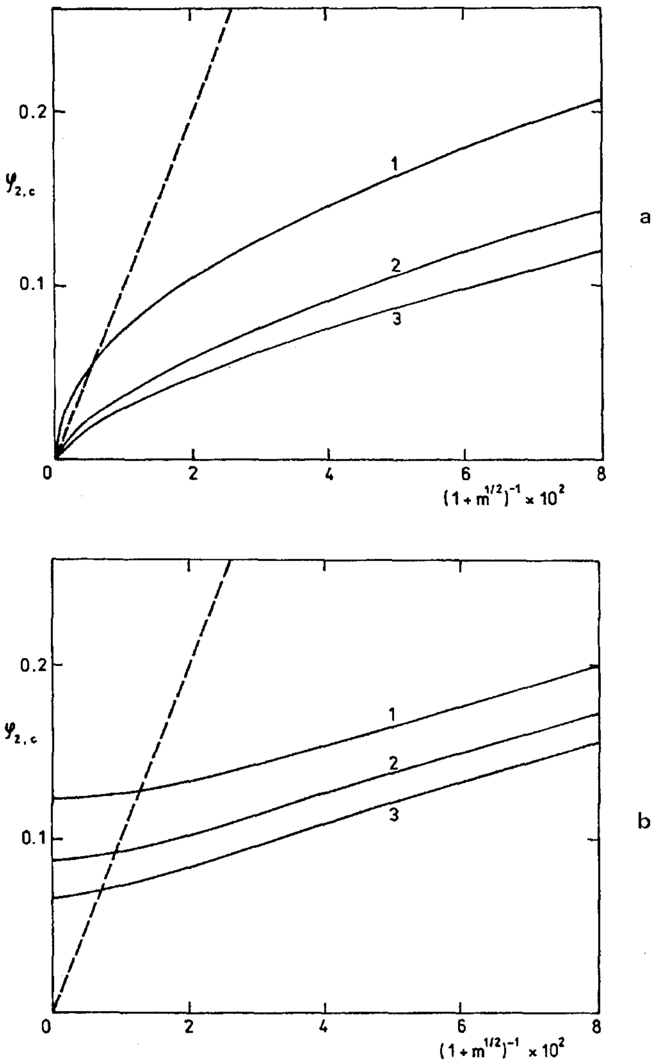

Figure 1: Chain length dependence of the critical volume fraction $\varphi_{2,c}$
(a) $\nu_c = 1/3$ and $\zeta_c = 1/4$, 0 and -1/4 (curves 1 to 3). (b) $\nu_c = 0.4$ and $\zeta_c = 0.1$, 0 and -0.1 (curves 1 to 3). Broken curves in both panels for $\nu_c = 0$ and $\zeta_c = 0$ (classic theory).

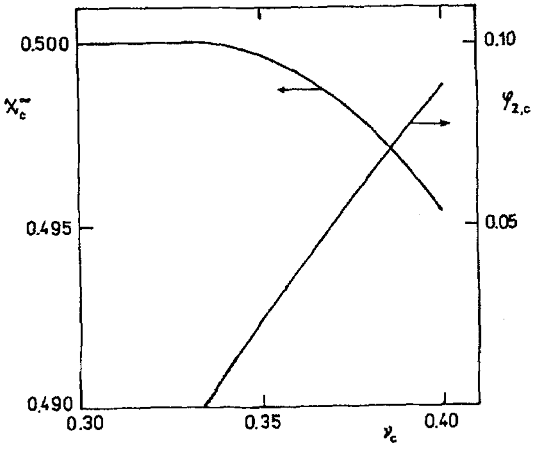

Figure 2: Dependence on ν_c of the critical parameters. Left scale χ_c^∞, right scale $\varphi_{2,c}^\infty$.

by the classic theory (where both ν and ζ are set equal to zero). It can be computed by numerically solving the equation

$$(\varphi_{1,c}^{\infty})^{-2} - 3\nu_c - 8\zeta_c\varphi_{2,c}^{\infty} = 0 \qquad (13)$$

which obtains from eq (12) for 1/m=0 (Fig. 2). For $\zeta_c = 0$, eq (13) simplifies to

$$\varphi_{2,c}^{\infty} = 1 - (3\nu_c)^{-1/2} \qquad (14)$$

As shown by Fig. 1 the critical concentrations at $\nu_c > 1/3$ are less dependent on the chain length than at $\nu_c < 1/3$.

For given values of ν_c, ζ_c, and $\varphi_{2,c}$, the critical value of χ_c can be computed from the relation [7]

$$\chi_c = (1/2)(1 - \varphi_{2,c})^{-2} - 3\nu_c\varphi_{2,c} - 6\zeta_c\varphi_{2,c}^2 \qquad (15)$$

Fig. 3a presents the dependences of χ_c vs $(1 + m^{-1/2})^2$ for several values of ν_c, the ζ_c parameter being set equal to zero, for simplicity. At $\nu_c \leq 1/3$, the χ_c^∞ value is always equal to 1/2 whereas at $\nu_c > 1/3$ it is lower than this. There exists the value m* (depending on ν_c) below which χ_c for finite chains drops below 1/2.

It can be seen from Figs 2 and 3b that χ_c^∞ is the lower the higher $\nu_c > 1/3$. It is also noteworthy that the plots of χ_c vs $(1 + m^{-1/2})$ for $\nu_c > 0$ have lower slopes than for $\nu_c = 0$. Fig. 3b shows that, for $\nu_c > 1/3$, the χ_c^∞ values become closer to 1/2 with negative ζ_c and more remote from 1/2 for positive ones.

The plot of χ_c vs $(1 + m^{-1/2})^2$ according to eqs (3) and (4) is equivalent to the plot of $1/T_c$ vs $M^{-1/2}$ (cf. eq(8)). It follows from Fig. 3 that both of them should be exactly linear at $\nu_c = 0$ and approximately so for $\nu_c \lesssim 0.2$. If ν_c approaches or exceeds 1/3 the plot should be curved. If a section of the curve for $\nu_c \leq 1/3$ were fitted by a straight line,

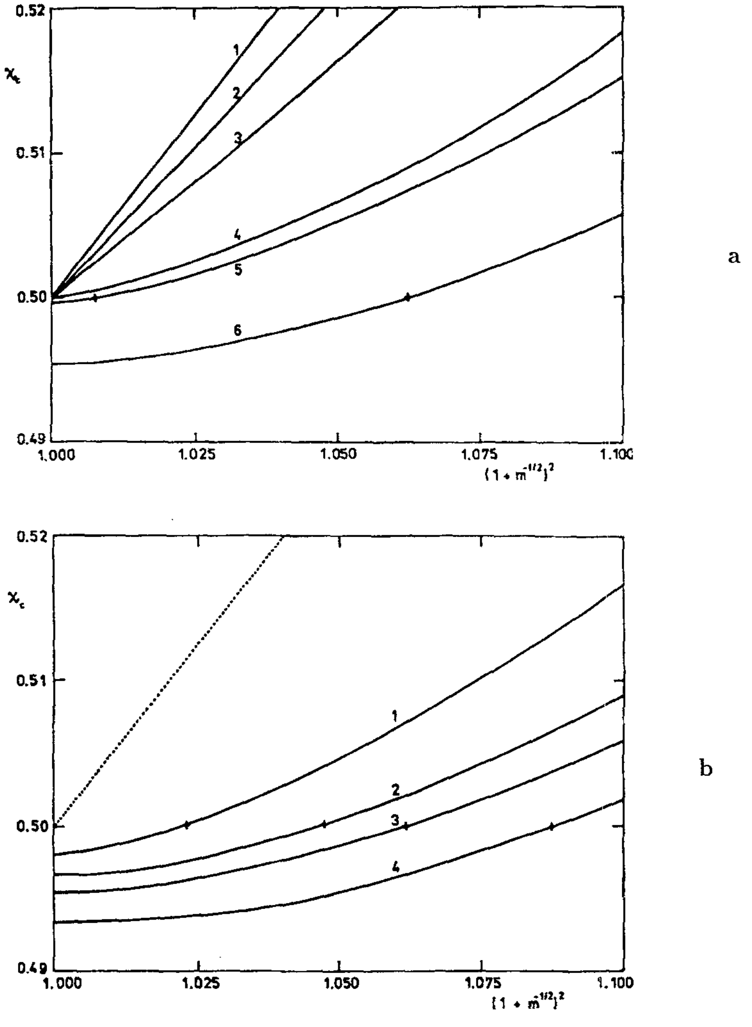

Figure 3: Chain length dependence of the critical value of χ
(a) Curves 1 to 6 for $\nu_c = 0$, 0.1, 0.2, 1/3, 0.35 and 0.4 with $\zeta_c = 0$. (b) Curves 1 to 4 for $\nu_c = 0.4$ with $\zeta_c = -0.5$, -0.1, 0, 0.1. Crosses denote m*.

extrapolation would necessarily lead to $\chi_c^\infty < 1/2$ and to an underestimation of Θ_L^{PE} (if $\psi < 0$) or to an overestimation of Θ_u^{PE} (if $\psi > 0$). Then, the Θ^{PE} temperatures differ from the Θ^A values. In this case the difference is an artifact. It may, however, be a real one if $\nu > 1/3$. Here, the χ_c values for long enough chains ($m > m^*$) are lower than 1/2 and, hence, the corresponding critical temperatures T_c are higher than Θ_U^A or lower than Θ_L^A.

Fig. 3 shows that the slope of the dependence of χ_c on $(1+m^{-1/2})^2$ is equal to unity only for $\nu = 0$. As ν increases the dependences become non-linear and the slopes of the initial tangents or of linear approximation to the curves are lower than unity. Fitting, e.g., the initial part of the curves by the approximate formula

$$\chi_c \simeq \chi_c^\infty + p(m^{-1/2} + \frac{1}{2}m^{-1}) \tag{16}$$

(which for p=1 goes over into eq (4)) and assuming eq (6) to be valid, we obtain

$$1/T_c = 1/\Theta + p(\psi\Theta)^{-1}m^{-1/2} \tag{17}$$

The slope S of the plot of $1/T_c$ vs $1/m^{1/2}$ is

$$S = p(\psi\Theta)^{-1} \tag{18}$$

Hence, the values of ψ obtained by means of eq (8) are p times higher than those calculated with eq (18). The well known differences [2-5] in ψ values estimated by the standard procedure from the critical points and from dilute solution properties (second virial coefficient, intrinsic viscosity) may thus be explained.

It is to be emphasized that these results offer merely a very simple, qualitative suggestion to explain the differences in Θ and ψ because the parameters ν and ζ are assumed to be independent of temperature. We also must not neglect the fact that the plots of $1/T_c$ vs $1/M^{1/2}$ for solutions of polymers (mostly non-polar), which have been investigated so far, are linear and seemingly support the original form of the theory. This probably results from a compensation of several factors at the critical point because a quantitative fit by the Shultz-Flory equation of the entire cloud point curves can be achieved only if the χ parameter is treated as a rather involved function of T, φ_2 and m [9].

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