polymer papers

Coexistence curve of semidilute polymer solutions

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By using the interaction parameters deduced from small-angle neutron and X-ray scattering, we have calculated, via mean-field theory, the coexistence curve of the semidilute solutions of polystyrene in cyclohexane. We obtain substantial agreement between the theoretical coexistence curve and the observed phase-separation points reported in the literature. General features of the temperature–concentration diagram of polymer solutions in the semidilute poor solvent regime are also discussed.

(Keywords: coexistence curve; semidilute solutions; poor solvent regime; polystyrene; cyclohexane; small-angle neutron scattering; small-angle X-ray scattering)

INTRODUCTION

One of the chief achievements of the modern theory of polymer solutions over the last 20 years is the recognition that semidilute solutions are remarkably simple to understand[1]. For the case of good solvent systems, scaling ideas have proved to work quite well in explaining various experimental results[1]. However, for the case of poor solvent systems, there still remain some controversial points regarding the temperature–concentration diagrams[2-4]. The purpose of the present paper is to discuss the coexistence curve of semidilute solutions of polystyrene in cyclohexane, thereby clarifying the general features of temperature–concentration diagrams of polymer solutions in the semidilute poor solvent regime. We calculate theoretically the semidilute branch of the coexistence curve of polystyrene in cyclohexane by using the interaction parameters obtained by small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS), and compare it with the experimental phase-separation points reported in the literature. In calculating the theoretical coexistence curve we use perturbation theory in the mean-field approximation, which is considered to work rather well in the regime considered[1].

INTERACTION PARAMETERS

Criterion for semidilute poor solvent regime

Let us begin by establishing the condition under which a semidilute solution is said to be a poor solvent system. For this purpose it will be helpful to recall the case of dilute solutions. As is well known, the poor solvent condition for a dilute solution is given by[1]:

$$Z_1 \equiv (\beta_1/b^3)\sqrt{N} < 1 \tag{1}$$

where b is the root-mean-square length of a polymer segment, N the number of segments contained in a polymer chain and β_1 the binary cluster integral (excluded volume) between polymer segments in solution. The physical meaning of the above inequality is that the total excluded volume of segments in a polymer chain ($\simeq \beta_1 N^2$) is smaller than the volume of the polymer coil R_G^3, where $R_G \simeq N^{1/2}b$ is the unperturbed radius of gyration of a polymer chain. The same argument applies to the three-body interaction among segments. Let β_2 be the ternary cluster integral of the three-body interaction. Then the total excluded volume of three-body contacts in a polymer chain is given by $\beta_2 N^3$. Requiring that this must be small compared with $R_G^6 \simeq (Nb^2)^3$, we obtain an inequality:

$$Z_2 \equiv (\beta_2/b^6) < 1 \tag{2}$$

The poor solvent condition for a semidilute solution is given by a similar argument. Here we must note the fact that, in the case of semidilute solutions in which polymer chains fully overlap one another, the correlation of segments in a polymer chain is screened to a length ξ by the presence of segments belonging to other polymer chains[5]. Let us define the number of segments g contained in that part of a polymer chain whose mean square length is just ξ^2 by the relation:

$$\xi^2 = gb^2 \tag{3}$$

Then the poor solvent condition in the semidilute case may be stated as follows: the total excluded volume within the part of a polymer chain having g segments ($\simeq \beta_1 g^2$) must be smaller than the volume ξ^3. By using the Edwards formula[5] for ξ:

$$\xi \simeq b/\sqrt{(\rho\beta_1)} \tag{4}$$

we have:

$$\beta_1/b^6\rho < 1 \tag{5}$$

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This is the required condition for a semidilute poor solvent system. In a semidilute solution, the crossover from poor to good solvent regime occurs at:

$$\beta_1/b^6\rho = 1 \tag{6}$$

It must be remarked here that the poor solvent condition with respect to three-body interaction is given by the inequality (2) both for dilute and semidilute cases, as we can infer from the fact that the left-hand side of the inequality does not contain N. It can be shown[6] that the inequalities (5) and (2) are equivalent to the Ginzburg–Kadanoff criterion[7] for the applicability of a mean-field approximation to the segment distribution in semidilute solutions.

Scattering function and interaction parameters

In a previous paper[8] we have analysed SANS from semidilute polymer solutions in the poor solvent regime. By a cluster expansion method in which only the contributions of series diagrams are taken into account, the scattering function $G(q)$, q being the momentum transfer of the scattering vector, is calculated as[8]:

$$G(q) = \frac{G_0(q)}{1 + (\beta_1\rho + 3\beta_2\rho^2)G_0(q)} \tag{7}$$

where $G_0(q)$ is the scattering function of an unperturbed Gaussian chain. We are concerned with the intermediate momentum range:

$$R_G^{-1} < q < b^{-1} \tag{8}$$

In this case $G_0(q)$ can be approximated as:

$$G_0(q)^{-1} = \frac{b^2}{12}\left(q^2 + \frac{6}{Nb^2}\right) \tag{9}$$

and we have a Lorentzian scattering law:

$$G(q) = \frac{12}{b^2}\left(\frac{1}{q^2 + \xi^{-2}}\right) \tag{10}$$

where the correlation length (the screening length) ξ is given by:

$$\xi^{-2} = \frac{6}{Nb^2} + \frac{12}{b^2}\beta_1\rho + \frac{36}{b^2}\beta_2\rho^2 \tag{11}$$

Equation (10) together with equation (11) were obtained by several authors[8-10]. Since the quantities associated with polymer segments N, b, β_1, β_2 and ρ are not uniquely defined, we use measurable quantities M, A, B_1, B_2 and c defined respectively as follows:

$$MA^2 = Nb^2 \qquad M^2B_1 = N^2\beta_1 \qquad M^3B_2 = N^3\beta_2 \qquad (c/M)N_A = \rho/N \tag{12}$$

where M is the molecular weight of a polymer molecule, N_A is Avogadro's number and c is the weight concentration of the solution. Then the angular dependence of the scattered intensity $I(q)$ is given by:

$$I(q) = I(0)(1 + \xi^2 q^2)^{-1} \tag{13}$$

$$\xi^{-2} = \frac{6}{MA^2} + 12N_A\frac{B_1}{A^2}c + 36N_A^2\frac{B_2}{A^2}c^2 \tag{14}$$

In the preceding work[8] we have measured the angular dependence of the intensity of SANS by semidilute solutions of polystyrene in deuterated cyclohexane in the temperature range from 31.5 to 43°C. The measured $I(q)$ obeyed equation (13), and we obtained ξ as a function of concentration and temperature. From the concentration dependence of ξ thus determined, we deduced the interaction parameters B_1 and B_2 via equation (14). Here we have used the value: $A = 0.7$ Å. It was found that B_1 changes its sign at about 40°C, the θ temperature, and in the vicinity of this point the temperature dependence of B_1 can be expressed as:

$$B_1 = 6 \times 10^{-27}\,\tau\ \mathrm{cm}^3 \qquad (-3 \times 10^{-2} < \tau < 1 \times 10^{-2}) \tag{15}$$

where the reduced temperature τ is defined by:

$$\tau = 1 - \theta/T \tag{16}$$

On the other hand, near the θ point, B_2 is almost independent of temperature and has a value:

$$B_2 = 0.8 \times 10^{-51}\ \mathrm{cm}^6 \tag{17}$$

In order to get the interaction parameters for polystyrene in protonated cyclohexane, we have performed analogous SAXS measurements[11] and obtained essentially the same result as those of equations (15) and (17) except for the fact that the θ point in this case is about 35°C.

With these interaction parameters, the crossover line from poor to good solvent regime is calculated from equation (6) as:

$$\tau = 1.2 \times 10c \tag{18}$$

The following investigations are concerned with the cases within the poor solvent regime:

$$\tau < 1.2 \times 10c \tag{19}$$

Osmotic compressibility

Before going into the calculation of the coexistence curve, we would like to compare the above interaction parameters with the recent light-scattering experiment of Stepanek *et al.*[12] on high-molecular-weight polystyrene in cyclohexane, the molecular weight being as high as 2×10^7. These authors have found that the concentration dependence of the osmotic compressibility at the θ point is given by:

$$\frac{1}{c}\left(\frac{\partial\pi}{\partial c}\right)_\theta = 2.93 \times 10^7 c \tag{20}$$

They have also found that within about 1°C from the θ point the temperature dependence of the osmotic compressibility is given by:

$$\frac{(\partial\pi/\partial c)_\theta}{\partial\pi/\partial c}=1-0.97\times10^{-2}(\theta\tau/c) \qquad (21)$$

Let us derive corresponding equations theoretically. From the compressibility equation:

$$kT(\partial\pi/\partial c)^{-1}=G(q=0) \qquad (22)$$

together with equations (10) and (11), we have

$$\frac{1}{N_A kT}\frac{\partial\pi}{\partial c}=B_1N_Ac+3B_2N_A^2c^2 \qquad (23)$$

In deriving this equation we have neglected the term containing $1/M$, which is allowed for the high-molecular-weight sample under discussion. Substituting the SANS–SAXS values of B_1 and B_2, equations (15) and (17) respectively, into the above equation we obtain:

$$\frac{1}{c}\left(\frac{\partial\pi}{\partial c}\right)_\theta=2.2\times10^7\,c \qquad (24)$$

and

$$\frac{(\partial\pi/\partial c)_\theta}{\partial\pi/\partial c}\simeq1-1.4\times10^{-2}(\theta\tau/c) \qquad (25)$$

These equations should be compared with empirical formulae (20) and (21). We see that a rather good agreement is obtained. This shows the validity of the interaction parameters obtained through our analysis of SANS and SAXS measurements.

COEXISTENCE CURVE IN SEMIDILUTE RANGE

In general, a theoretical coexistence curve (binodal curve) is obtained by requiring simultaneously the equality of the osmotic pressures and the equality of the chemical potentials of the coexisting phases. However, as pointed out by de Gennes[1], for the purpose of obtaining the semidilute branch of the coexistence curve, the first condition alone is sufficient, because the osmotic pressure of a dilute phase is very small. Therefore the semidilute branch of the coexistence curve is determined simply by imposing the condition that the osmotic pressure as a function of the concentration is zero:

$$\pi(\rho)=0 \qquad (26)$$

Another simplifying situation is that in the semidilute poor solvent regime the mean-field description of osmotic pressure:

$$\frac{\pi}{kT}=\frac{\rho}{N}+\tfrac{1}{2}\beta_1\rho^2+\beta_2\rho^3 \qquad (27)$$

is adequate[1]. Combining the two equations we obtain the theoretical coexistence curve in the semidilute range:

$$1/N+\tfrac{1}{2}\beta_1\rho+\beta_2\rho^2=0 \qquad (28)$$

or in terms of the observable quantities we have:

$$1/M+\tfrac{1}{2}B_1N_AC+B_2N_A^2C^2=0 \qquad (29)$$

Defining

$$\tilde{\tau}\equiv(\sqrt{M})\tau \qquad \tilde{c}\equiv(\sqrt{M})c \qquad (30)$$

and using the interaction parameters as determined by SANS and SAXS measurements, equations (15) and (17), we obtain:

$$\tilde{\tau}=-5.6\times10^2(1/\tilde{c})-0.16\,\tilde{c} \qquad (31)$$

In *Figure 1* we show this theoretical coexistence curve together with the observed phase-separation points for polystyrene–cyclohexane systems reported by several authors. Here the $\tilde{\tau}$ values of experimental phase-separation points were calculated by taking θ as 35°C.

DISCUSSION

By using the thermodynamic parameters obtained by SANS and SAXS experiments, we have calculated via mean-field approximation the semidilute branch of the coexistence curve of polystyrene in cyclohexane and compared it with some direct observations of phase-separation points reported in the literature. The result is moderately successful: the theoretical curve reproduced rather well the overall feature of the experimental phase-separation temperatures in the semidilute range, although there remains a slight discrepancy between them. Again this substantiates the validity of our approach. A possible reason for the discrepancy might be the inaccuracy in locating the θ point through the measurement of binary cluster integral B, by SANS and SAXS.

At this point we should remark on the theory of Daoud and Jannink[2] on the temperature–concentration diagram of polymer solutions. In particular, these authors assumed that the line symmetric to the crossover line separating the poor and good solvent regimes is the asymptote of the semidilute branch of the coexistence curve. The present analysis shows that this is not the case,

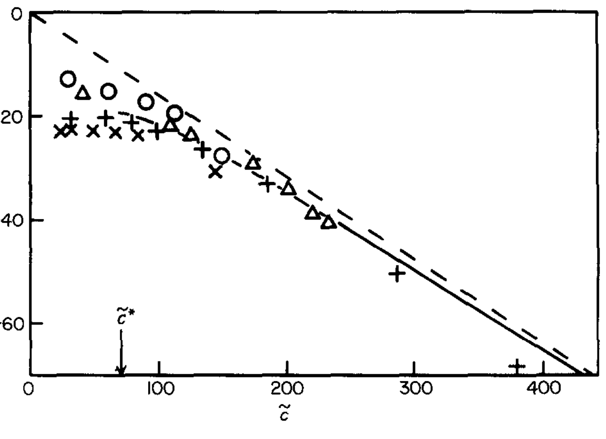

Figure 1 Theoretical coexistence curve (———) and the experimental phase-separation points: (○) Shultz and Flory[15], $M=2.5\times10^5$; (△) Shultz and Flory[15], $M=1.27\times10^6$; (+) Dobashi *et al.*[16], $M=1.56\times10^6$; (×) Saeki *et al.*[17], $M=2.7\times10^6$. Also shown is the asymptote (-----) to the theoretical coexistence curve. $\tilde{c}^*$ denotes the reduced crossover concentration from dilute to semidilute regime

contrary to the conclusion drawn from SANS measurements by Cotton *et al.*[13]. Indeed we found that the line symmetric to the crossover line is given by:

$$\tau = -1.2 \times 10c \tag{32}$$

whereas the asymptote of the coexistence curve is:

$$\tau = -1.6 \times 10^{-1} c \tag{33}$$

The conclusion reached by Cotton *et al.* is based on the proposal that the crossover line from poor to good solvent regimes is given by:

$$\tau \simeq 1 \times 10^{-1} c \tag{34}$$

which makes a sharp contrast to equation (18). We share the view[3,4,14] that the crossover line proposed by Cotton *et al.* actually corresponds to a gradual change in the right-hand side of equations (11) and (14) from the region where the third term is dominant to the region where the second term is superior. The 'crossover' line of this gradual change may be defined by equating the second and third terms of equations (11) and (14). By using our interaction parameters this line is calculated as:

$$\tau = 2.4 \times 10^{-1} c \tag{35}$$

This roughly agrees with equation (34) deduced by Cotton *et al.*

Essentially the same statement can be made on the recent analysis of the light-scattering experiment by Stepanek *et al.*[12] who, from the temperature dependence of the osmotic compressibility, have drawn the same conclusion as Cotton *et al.*

Finally we would like to remark on the compensation line, on which the excluded-volume effect of a semi-dilute solution essentially vanishes. This line corresponds to the situation that the second and third terms on the right-hand side of equations (11) and (14) cancel each other, and is given by[8]:

$$\tau = -2.4 \times 10^{-1} c \tag{36}$$

which is symmetric to equation (35). We now recognize that this line lies well below the coexistence curve and hence we cannot realize the ideal state of semidilute polymer solutions in equilibrium.

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