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Special features of water soluble polymers

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Abstract

Well below the conventional θ point, a polymer solution separates into a dense phase in equilibrium with a very dilute solution of collapsed coils. In the present note, considering the general structure of the energy of mixing, we predict a different type of coexistence curves (below another limiting point $\bar{\theta}$) where a dense phase (volume fraction $\phi = \phi_+$) is in equilibrium with a very dilute system of swollen coils $\phi = \phi_l \cong \exp(-\varepsilon N)$ [N : degree of polymerisation]. A good candidate for this behavior is the system p-oxyethylene / water, at room temperature.The dilute "solutions" used in drag reduction ($\phi \sim 10^{-4}$, $N \sim 10^4$) may in fact be mixtures of the phases ϕ_l and ϕ_+ as first suggested by Polik and Burchard from their light scattering data. The (ϕ_+) phase would also play a role in the adsorption of POE from water onto solid surfaces, and in various problems of colloid protection. Similar features could occur for many water soluble polymers which tend to form multistranded helixes or microcrystals.

THERMODYNAMICS

If the interaction between two monomers, in a solvent S, is repulsive, the solvent is usually considered to be good. However, it may happen that, at the same time, the interactions inside a larger group of monomers become attractive. For instance, with p.oxyethylene in water at room temperature, it could be that two strands (or more) tend to form helical portions of low energy. Or it may be that microcrystals are formed, from a small number of strands. We want to analyse the thermodynamics of these situations, starting from a generalised form of the Flory Huggins theory (1).

1) The standard Flory Huggins free energy F (per site, for a lattice model) is (as a function of the polymer fraction ϕ) :

$$\frac{F}{kT} = \frac{1}{N}\,\phi \ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \tag{1}$$

where χ (measuring the enthalpy of mixing) is, for the moment, taken to be constant. (N is the number of monomers per chain). Many features of eq. (1) can be understood rapidly by going to the limit $N \to \infty$ ($F \to F_\infty$). The plots of $F_\infty(\phi)$ are shown on fig. 1. If $\chi < 1/2$, the plot is always convex, and the solution remains a single phase. If $\chi > 1/2$, we expect an equilibrium between a phase of finite concentration ϕ_c, and a very dilute phase (ϕ_l). The special temperature at which $\chi = 1/2$ is the Flory θ point. The coexistence curve has the aspect shown on fig. 2a.

2) Consider now a more general form :

$$\frac{F}{kT} = \frac{\phi}{N} \ln\phi + (1-\phi)\ln(1-\phi) + \Delta_T(\phi) \tag{2}$$

where the reduced enthalpy of mixing $\Delta_T(\phi)$ incorporates the associations present at high ϕ,

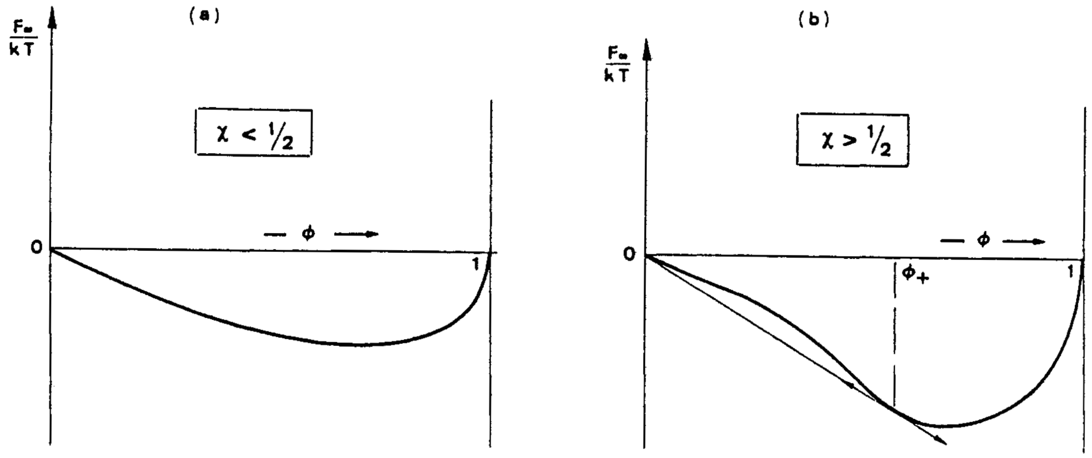

Fig. 1. Plots of free energy (per monomer volume) F as a function of the polymer fraction ϕ. Here only the limit of large molecular weights ($N \to \infty$) is representated.

a) Flory Huggins plot with $\chi < 1/2$: complete miscibility.
b) Same plot with $\chi > 1/2$: equilibrium between a phase (ϕ_+) and a very dilute phase.

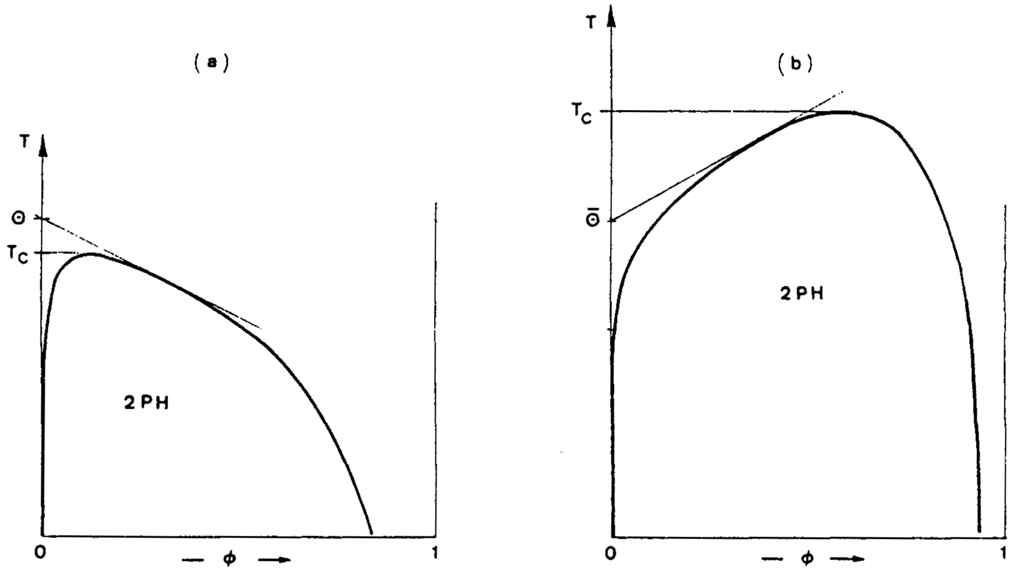

Fig . 2. Coexistence curves in the vicinity of : a) a normal θ point. b) a θ point.

and has the following features :

- $\Delta_T(\phi)$ is continuous and differentiable.
- $\Delta_T(1) = 0$.
- At low ϕ, $\Delta_T(\phi)$ has the Flory form :

$$\Delta_T(\phi \to 0) = \Delta'_0\,\phi - \chi_0\,\phi^2 + 0\,(\phi^3) \tag{3}$$

where $\chi_0 = \chi_0(T)$ depends only on temperature. Let us now focus our attention on the case where $\chi_0 < 1/2$ in the temperature range of interest, and concentrate again on the limit $N \to \infty$. The plot of $F_\infty(T)$ is convex at low ϕ (since $\chi_0 < 1/2$) and is convex at $\phi = 1$ (because of the term $(1-\phi)\ln(1-\phi)$ in eq. 2). However, when we reduce the temperature below a certain limit T_c , it may become concave at intermediate ϕ values (fig. 3a), and we expect an equilibrium between two phases ϕ_+ and ϕ_- , both of finite concentration.

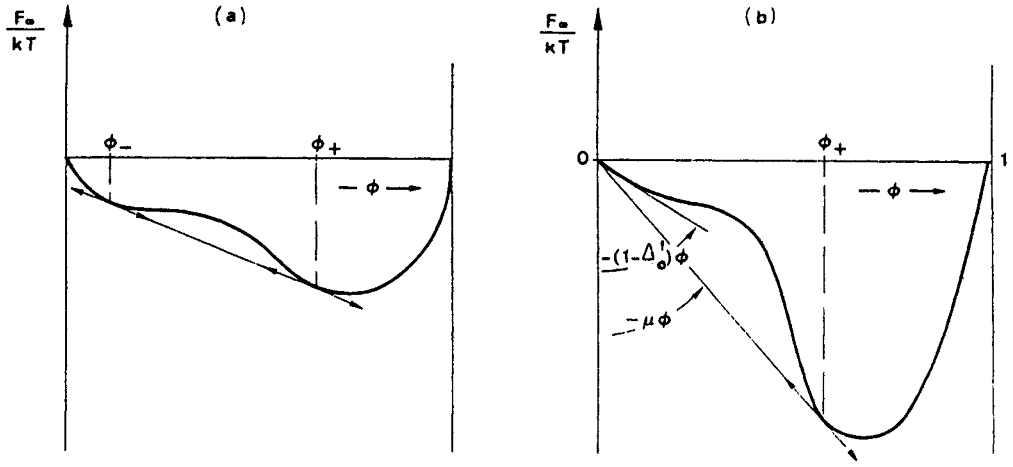

Fig. 3. Free energy plots as in fig. 1, but with an enthalpy of mixing which becomes attractive at high polymer concentration (a) $T > \bar{\theta}$: coexistence between two concentrated phases. (b) $T < \bar{\theta}$: coexistence between one concentrated and one very dilute phase.

If we decrease the temperature more ($T < \bar{\theta}$), we reach the situation of fig. (3b), where the equilibrium occurs between a concentrated phase ϕ_+ and a very small concentration ϕ_l. We determine ϕ_l by returning to the full form of the free energy F (eq. 2), and find :

$$\left.\begin{array}{l} \phi_l = \exp - (1 + N\varepsilon) \\ \\ \varepsilon = \mu - (1 - \Delta_0') \end{array}\right\} \qquad (4)$$

where $-\mu$ is the slope of the convex envelope defined on fig. 3b. Eq. 4 holds for $\varepsilon > 0$, i.e. at temperatures T below a certain value $\bar{\theta}$, defined by $\mu(\bar{\theta}) = 1 - \chi_0(\bar{\theta})$. The resulting aspect of the coexistence curve is shown on fig. 2b.

An important difference between the θ point and the $\bar{\theta}$ point is related to the state of the coils in the (ϕ_l) phase : below the θ point, they are collapsed (and in fact ϕ_l as computed from Flory Huggins theory, would be incorrect). Below the θ point, they are swollen (and to leading order in N, eq. 4 is good).

We have presented this discussion for a "normal" situation where $\Delta_T(\phi_+)$ becomes more negative when T is decreased. Of course, we may also have "inverted" situations where the diagrams of fig. 2 are turned upside down. The basic parameters are always χ_0 (T) and μ (T) : each of them may be an increasing or decreasing function of temperature.

PHYSICAL CONJECTURES

There are indications that solutions of POE in water near room temperatures have good solvent features at low ϕ, and bad solvent features at high ϕ (2). We are thus led to postulate that, say in the range 0° - 80° C, the phase diagram of the solutions is of the type shown on fig. 2b with a point $\bar{\theta}$ above room temperature. At higher temperatures (102° C) we also have an inverted θ point which is well known (3), but which needs not concern us here.

This should have interesting consequences :

1) At large N and finite ε, the concentration ϕ_l is expected to be very small (see eq. 4). Thus a nominal "solution" of concentration ϕ would actually be a mixture of two phases : one (ϕ_l) with very dilute, swollen coils, and one (ϕ_+) with concentrated polymers. This is exactly what has

been proposed by Polik and Burchard (4) from light scattering data. They call the ϕ_+ phase a gel : this suggests that, in the case of POE, helical (or crystalline) associations freeze the disentanglements. As regards the drag reduction, it is not clear wether it is due primarily to the dilute phase, or to the dilaceration of (ϕ_+) droplets by the turbulent shear fields.

2) Adsorbed POE is often used as a protective agent for colloids (5). Thus it is interesting to understand the possible role of the ϕ_+ phase in adsorption layers.

a) If the solid surface attracts the polymer at all ϕ, we expect no dramatic modification of the adsorption profile $\phi(z)$ (where z is the distance to the wall) : only a small modification in the inner region where $\phi(z) \sim \phi_+$. But the reptation motions inside the layer (7) might be blocked.

b) It could also happen that the solid attracts the polymer only when ϕ is below a certain limit ϕ_l : for instance, if the (ϕ_+) phase is made of helical polymers, these helixes could be repelled by the wall. Then the adsorption profile $\phi(z)$ is probably truncated at $\phi = \phi_l$.

In all cases, when we study the force between two parallel plates carrying adsorbed polymer layers, we expect that, at high compression, the relative weight of the (ϕ_+) phase will increase. This could lead to strong hysteresis effects (especially if helical conformations are involved). Indeed, the force distance law for mica / POE + water / mica is anomalously hysteretic (6).

To summarize : the $\bar{\theta}$ behaviour should be observable in a number of polymer / solvent systems, and could have important consequences for colloid protection. For the particular case of POE / water, from the observations of Polik and Burchard, we expect that $\bar{\theta}$ is around 70° C, and T_c is a few degrees higher. It may be that the rates of exchange between (ϕ_+) and (ϕ_-) above $\bar{\theta}$ (or between ϕ_+ and ϕ_1 below $\bar{\theta}$), are very slow : then to display the full phase equilibrium would require measurements over very long times.

The same scheme may turn out to be also applicable to other water-soluble polymers, such as the polysaccharides, which are well known for their complex association forms (8). It may even be relevant for certain mixtures of polymer plus organic solvent, such as those which are used for gel-spinning. But we need much more thermodynamic data to assess these points.

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