# Symmetric and Nonsymmetric Tricritical Points in Liquid Sulfur Solutions

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The dilute $n \rightarrow 0$ vector model, recently used to model the phase equilibria in sulfur solutions and living polymers, possesses a nonsymmetrical tricritical point of the sort found in three- and more-component solutions at a small nonzero value of the magnetic field as well as the symmetric tricritical point at zero field. This has interesting consequences for the phase diagrams of sulfur solutions and suggests a resolution of a number of discrepancies between the earlier (zero-field) theory of Scott and experiments on sulfur solutions.

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The phase diagrams of elemental sulfur dissolved in various organic solvents have interesting and unusual features. They exhibit[1-6] a high-temperature miscibility gap bounded below by a lower critical solution temperature (LCST) as well as the more familiar low-temperature miscibility gap surmounted by an upper critical solution temperature (UCST). Nearly twenty years ago Scott[4,5] proposed an elegant chemical equilibrium theory to explain these phase diagrams, based on the ideas of Flory,[7] Gee,[8] and Tobolsky and Eisenberg,[9] and studied these systems experimentally.[6]

Recently we have developed a nonclassical lattice solution model for the polymerization of sulfur[10-13] and sulfur solutions[13,14] as well as for living polymers[15] and have shown that it is identical to the $n \rightarrow 0$ limit of the $n$-vector model of magnetism, or in the case of solutions to an annealed dilute $n \rightarrow 0$ vector model. We showed that Scott's theory can be viewed as the mean-field approximation to the dilute $n \rightarrow 0$ vector model and that the LCST found by Scott corresponds to a (zero-field) symmetric tricritical point in the dilute magnet, analogous to that used by Blume, Emery and Griffiths[16] to model the phase separation in $^3$He-$^4$He mixtures at very low temperatures. Scott's theory contains an equilibrium constant $K_1$ for opening an $S_8$ ring to form a diradical $S_8$ chain, and an equilibrium constant $K_p$ for propagating a chain of $n$ $S_8$ units to a chain of $n+1$. Scott (and we) worked out the consequences of the theory for the phase diagrams of sulfur solutions in the limit $K_1 \rightarrow 0$. Since $K_1$ is believed to be of the order of $10^{-12}$ for pure sulfur near the transition, this seemed to be a sensible approximation.

Despite the very considerable success of Scott's theory, discrepancies with experiment remain. In the limit $K_1 \rightarrow 0$, the theory predicts that the coexistence curve is pointed rather than flat at the LCST with an effective critical exponent $\beta = 1$. While the phase diagrams of sulfur with some solvents do show a rather pointed coexistence curve, those with some other are very flat.[6] Moreover, all the coexistence curves show distinct rounding sufficiently near the LCST. The theory predicts the existence of three-phase equilibrium for certain choices of the energy parameters, but this has not been seen in any of the systems studied. Instead of three-phase equilibrium, a dramatic flattening of the high-$T$ coexistence curve was observed as the two coexistence curves approached one another. This effect is so dramatic that it calls for explanation on its own, apart from the disagreement with the theory. The theory predicts that if by variation of a parameter (such as pressure) one passes from a condition where both UCST and LCST exist to one in which no critical solution point exists, this should occur via three-phase equilibrium, but experiments on the pressure dependence of sulfur solution phase diagrams by Schneider[17] find no three-phase equilibrium but rather a smooth critical locus with a critical double point. Increasing $K_1$ from zero to a number of order $10^{-12}$ has no visible effect on the predicted phase diagrams nor upon the discrepancies between the theory and experiment.

In this Letter I suggest that all of these discrepancies may be simultaneously resolved by two observations; one about the model, the other about sulfur solutions. First, I have found that the model has a *nonsymmetric tricritical point*[18] of the sort found in ordinary three- and more-component solutions at a small nonzero value of the equilibrium constant $K_1$ (i.e., at a small magnetic field $h$) in addition to the symmetric tricritical point at $K_1 = 0$. For values of $K_1$ greater than this (nonsymmetric) tricritical value, three-phase equilibrium does not exist and the sequence of phase diagrams predicted by the theory is exactly that observed by Schneider.[17] Moreover, the resulting phase diagrams exhibit the dramatic flattening of high-temperature phase boundary when the LCST is close to the nonsymmetric tricritical point. However, the value of $K_1$ required (about $10^{-3}$) is gigantic compared to the value for pure sulfur ($\sim 10^{-12}$) and it is most unlikely that purely physical solvent or pressure effects could change $K_1$ by this amount.

The second observation is that chemical reaction of a small amount of the sulfur with the solvent can act as a *dopant*, drastically increasing the effective value of $K_1$. Recently we have considered the effect of deliberately doping pure sulfur with small amounts of halogens on the electron-spin-resonance (ESR) signal[19] and heat capacity[20] of pure sulfur. The effects can be understood as constraining the concentration of polymer *ends* at a certain value. This has the effect of drastically raising the effective value of the magnetic field in the corresponding magnetic model. Reaction of less than 1% of the $S_8$ rings (less than 0.13% of S atoms) is sufficient to increase $K_1$ beyond its (nonsymmetric) tricritical value.

In Fig. 1 I show the univariant features of the global phase diagram for various values of the magnetic field in the mean-field approximation. $\tilde{J}$ is the spin coupling constant of the magnet divided by $kT$ and, when multiplied by the coordination number $q$ of the lattice, plays the role of polymerization equilibrium constant $K_p$ of Scott's theory. $\tilde{K}$ is a microscopic energy of mixing divided by $kT$ and plays the same role in the two theories. The diagram is a projection along the axis of the chemical potential difference, $\mu_s - \mu_0$, between spins (or sulfur) and solvent. Curve $a$ is that for zero magnetic field, $h=0$, and is identical with Fig. 1 of Ref. 14 (to which the reader is referred for a more detailed discussion of the diagram and the correspondence between the magnet and polymer theories). The horizontal portion is the "ordinary" nonmagnetic critical locus for separation of unlike species. The downward-curving portion is the locus of tricritical points and the nearly straight dashed line joining them is the three-phase line. Also shown (dotted line) is the locus of critical end points at which the magnetic critical locus intersects the first-order phase separation. For $h$ nonzero, no matter how small, the critical end-point line ceases to exist and the downward-curving line ceases to be a line of tricritical points and becomes instead a line of (wing) critical points. The situation is then one familiar in the study of nonsymmetrical tricritical points[18]: two critical loci, each of which ends in a critical end point, these critical end points being connected by a line of three-phase equilibrium. As the field $h$ is increased, the three-phase line shrinks in length until the critical end points meet at a tricritical point at which all three phases are in critical equilibrium. For larger values of $h$ only a single continuous critical locus exists. Curves $b$, $c$, and $d$ in Fig. 1 are for $h=0.01$, 0.05, and 0.10, respectively. The tricritical point occurs at $h=0.0469$, $q\tilde{J}=1.358$, $q\tilde{K}=3.895$ with $m=0.129$ and $x_s=0.595$, where $h=H/kT$ and $H$ is the magnetic field of the magnet, $m$ is the magnetization per site, and $x_s \equiv \phi_s$ is the fraction of sites occupied by spins (volume fraction of sulfur). According to the correspondence[14] between magnet and sulfur, the fraction of $S_8$ rings which have reacted with solvent at the tricritical point is given by $\frac{1}{2}hm/x_s \cong 0.005$.

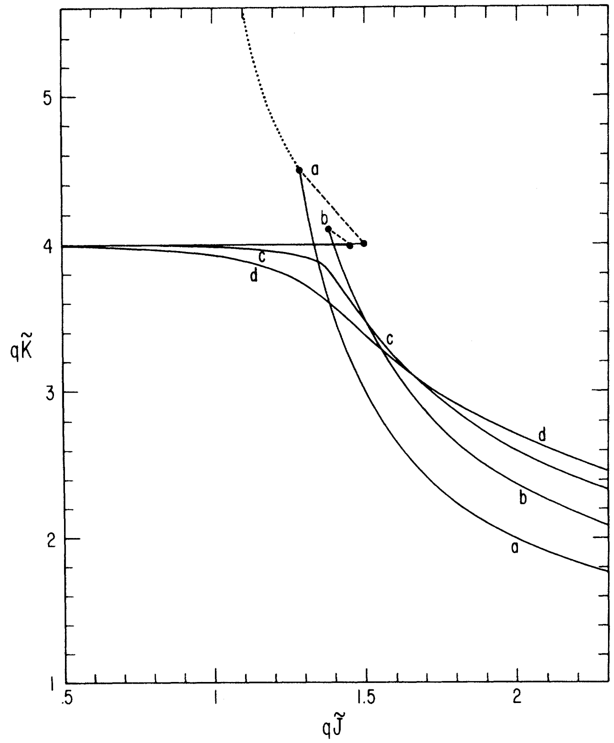

FIG. 1. Phase diagram for dilute $n \rightarrow 0$ vector model in zero and nonzero fields. Curve $a$, $h=H/kT=0$; curve $b$, $h=0.01$; curve $c$, $h=0.05$; curve $d$, $h=0.1$.

As described in Ref. 14, a given sulfur solution is characterized by a fixed value of $T_1/T_p$ where $T_1$ is the UCST in the absence of any polymerization ($K_1 \equiv 0$) and corresponds to $q\tilde{K}=4$, and where $T_p$ is the polymerization temperature of pure sulfur, 432 K. As the temperature of the solution is varied the system moves along curving path in the $\tilde{J},\tilde{K}$ plane described by the Arrhenius form

$$q\tilde{J} = K_p(T) = \exp\left[\frac{\Delta H_p}{RT_p}\left(1 - \frac{T_p}{T_1}\frac{q\tilde{K}}{4}\right)\right], \qquad (1)$$

where, following Scott, I have used the value $\Delta H_p/RT_p = 2.70$. As $T$ of the solution increases, $\tilde{K}$ decreases but $\tilde{J}$ increases, the system sweeping along a curve from the upper left to lower right of Fig. 1 (see, for example, curves 5–8 of Fig. 1, Ref. 14). Thus, for $h$ greater than the tricritical values, the system may either remain in the two-phase region, cut through into the one-phase region for some interval, or graze the critical curve at a critical double point.

In Fig. 2, three coexistence curves for $h = 0.05$ are shown. Curves $a$, $b$, and $c$ correspond to $T_1/T_p = 1.0$, 1.055, and 1.10, respectively. The dashed curve represents the polymerization transition line in the limit $K_1 \rightarrow 0$ (i.e., $\tilde{J}_s \phi_s K_p = 1$). For $h > 0$ the transition is no longer sharp, but this curve gives a rough guide as to where polymerization becomes important. The dotted curve in Fig. 2 is the locus of critical points.

Several interesting features appear in this figure. First, as expected, there is no three-phase equilibrium. Rather, the critical locus is continuous and the coexistence curves move smoothly together and meet at the critical double point at $T/T_p = 1.086$ and $\phi_s = 0.554$, after which only a single miscibility gap exists. Secondly, the high-temperature coexistence curve is distinctly rounded at the LCST in reasonable qualitative agreement with the experimental curves and sharp contrast with the curves for $K_1 = 0$ or $10^{-12}$. Thirdly, when the critical temperatures are far apart as in curve $a$, the high-temperature curve retains a "memory" of the tricritical point and is more pointed at the LCST than is the low-temperature curve at the UCST. As the critical temperatures become closer, however, the high-$T$ curve loses all resemblance to the $K_1 = 0$ shape and becomes much flatter at the LCST than is the low-$T$ curve at the UCST. This is in striking agreement with the results of Larkin, Katz, and Scott,[6] who found that the most pointed curve occurred for sulfur-biphenyl with a ratio of $T_c$'s of 1.287, while the solutions of *cis*-decalin and *cis-trans* mixtures of decalin with sulfur gave very flat LCST's. The explanation for this phenomenon is to be found in the proximity of the LCST to the (nonsymmetric) tricritical point. The tricritical point occurs at $T/T_p = 1.09$, $x = 0.595$, and $h = 0.0469$, very close to the LCST. Indeed, by adjusting $h$ and $T_1/T_p$ we can arrange that LCST occurs exactly at the tricritical point. In this case the high-$T$ coexistence curve is described by the tricritical exponent $\beta$ appropriate when the composition $\phi_s = x$ couples to the order parameter; that is, $\beta_t = \frac{1}{4}$ rather than the usual classical value $\frac{1}{2}$. The flatness of the high-$T$ curve for $h = 0.05$ and $T_1/T_p = 1.055$ reflects the approach to this situation. This leads to the interesting possibility that Larkin, Katz, and Scott were in fact very close to observing a nonsymmetric tricritical point in their studies of decalin-sulfur solutions several years before this kind of tricritical point became a subject of intense study.

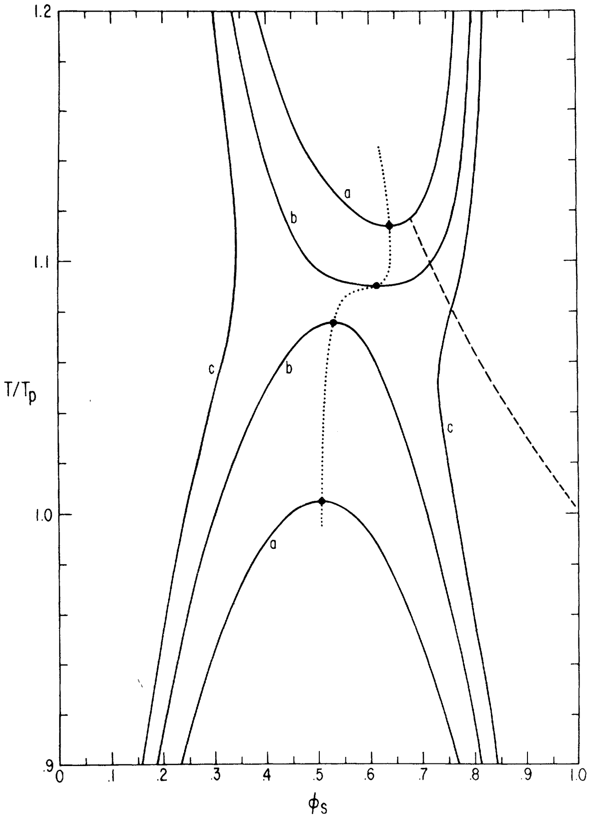

FIG. 2. Temperature-composition phase diagram for $h = 0.05$. Curves $a$, $b$, and $c$ correspond to $T_1/T_p = 1.0$, 1.055, and 1.10, respectively. Dashed line is the curve $K_p \phi_s = 1$, which is the polymerization transition line for $K_1 = 0$. Dotted curve is the critical locus.

The existence of the nonsymmetric tricritical point has interesting consequences for the phase diagram of "living polymer" solutions as well as for sulfur solutions. We have recently used the dilute $n \rightarrow 0$ vector model to predict the kinds of phase diagrams likely to be seen in these solutions.[12] These systems typically polymerize with decreasing rather than increasing temperature so that the resulting phase diagrams look more like those of the reference magnet than do those of sulfur. Analogous suppression of three-phase equilibrium and anomalous flattening of the phase boundary occurs in these systems. These results, details of the calculations leading to Figs. 1 and 2, and discussion of the effects of nonclassical critical fluctuations and polymeric rings will be presented elsewhere.

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