Phase equilibrium in ternary solutions containing two semiflexible polymers with different lengths

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Ternary phase diagrams were determined for solutions of bidisperse poly(hexyl isocyanate) (PHIC) and toluene. The larger the molecular weight ratio of the two polymer components, the wider the isotropic–liquid crystal biphasic region on the phase diagram. The ternary PHIC–toluene system did not exhibit an isotropic–liquid crystal–liquid crystal three-phase separation, in contrast with aqueous solutions of schizophyllan, a rodlike polysaccharide previously studied. The experimental results for the system PHIC and toluene, together with those for aqueous schizophyllan, were compared with the Khokhlov–Semenov theory extended by Odijk to bidisperse wormlike cylinders (KSO theory). Much better agreement with experiment was achieved for the KSO theory than for Abe and Flory's theory of bidisperse rods. However, the KSO theory failed to predict the three-phase separation.

(Keywords: ternary phase diagram; liquid crystal; semiflexible polymer; poly(hexyl isocyanate); schizophyllan)

INTRODUCTION

Abe and Flory[1] were the first to predict on the basis of the lattice model for rigid rods[2] that a ternary solution containing two rodlike polymers with different lengths would separate into two or three phases depending on the composition of the solution: an isotropic phase and an anisotropic phase (IA region); an isotropic phase and two anisotropic phases (IAA region); or two anisotropic phases (AA region). Thus a triangular phase diagram of this solution may possibly consist of five regions: isotropic solution region (I), IA region, IAA region, AA region and anisotropic solution region (A).

The qualitative feature of this prediction has been well substantiated with our recent phase equilibrium data for aqueous schizophyllan[3,4], a triple helical polysaccharide[5,6]. Particularly, those systems containing two polymers differing greatly in molecular weight exhibited both IAA and AA phase separations in addition to IA phase separation. However, the observed and theoretical phase diagrams differed greatly in quantitative terms[3,4]. This difference may be attributed, among other things, to the finite stiffness of the schizophyllan triple helix, which has not been taken into account in the Abe–Flory theory, although schizophyllan is known to be the stiffest polymer so far investigated, and is characterized by the wormlike chain model of Kratky and Porod with a persistence length q as large as 200 nm[5,6]. For the same reason, all the existing theories of rodlike polymers have failed to explain phase equilibrium data for binary solutions of schizophyllan[7,8] and other semiflexible polymers[9,10].

Khokhlov and Semenov[11,12] have developed a theory for persistent chains (identical to the Kratky–Porod wormlike chain) on the basis of the Onsager theory for rigid rods[13] and showed that the effect of finite stiffness on the phase diagram would be very appreciable for long chains. As shown in our previous paper[14] as well as in Odijk's review article[15], the existing phase equilibrium data for binary solutions of semiflexible polymers are consistent with this theoretical prediction provided that q is larger than about 30 nm.

Recently, Odijk[15] has extended the Khokhlov–Semenov theory to ternary systems containing two polymers with different lengths (KSO theory) and the results compare favourably with our schizophyllan data[3,4]. However, the comparison is limited only to the two sets of data for schizophyllan, which has a relatively large q, and the KSO theory may not be fully substantiated until it is tested with additional data preferably for polymers with different q. Indeed, the approximate nature of the KSO theory has been noted by Odijk himself[15].

To meet this requirement, we performed another phase equilibrium study on ternary solutions of narrow-distribution poly(hexyl isocyanate) (PHIC) in toluene. In this paper we present the results from these measurements and combine them with all the other data for ternary solutions of schizophyllan so far obtained[3,4,16] in order to test the validity of the KSO theory.

EXPERIMENTAL

Three samples of PHIC (Z-2, $M_w = 2.09 \times 10^4$, $M_z/M_w = 1.06$; K-2, $M_w = 6.8 \times 10^4$, $M_z/M_w = 1.02$; Z-20, $M_w = 24.4 \times 10^4$, $M_z/M_w = 1.05$) chosen from our stock[17] were used for the phase equilibrium measurements. Since they are very narrow in molecular-weight distribution, they are hereafter regarded as monodisperse. Appropriate amounts of the two samples were mixed with toluene in a calibrated stoppered tube and stirred thoroughly by a magnetic bar at 25°C to effect complete dissolution. The

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mixture was kept standing for more than one day without stirring at the same temperature for phase separation. To effect complete phase separation, the mixture was centrifuged at the same temperature. The separated phases were finally taken out and diluted with benzene. The polymer mixture in each solution was recovered by freeze-drying, weighed to estimate the polymer weight fraction w in the corresponding phase, and subjected to gel permeation chromatography (g.p.c.) analysis (for Z-2+Z-20 mixture) or viscometry (for K-2+Z-20 mixture) to determine the fraction ξ of the lower-molecular-weight sample in the polymer mixture; the volume Φ of the isotropic phase relative to the total solution volume was also determined. The binary phase diagram for the system K-2+toluene was also measured at 25°C. The detailed experimental procedures are similar to those employed in the previous studies[4,14].

RESULTS

Binary phase diagrams

Figure 1 shows a plot of w *versus* Φ for the system K-2+toluene at 25°C, where w is the polymer weight fraction in the original solution. The data points are seen to follow the straight line indicated and extrapolated with reasonable accuracy to $\Phi=1$ and 0, yielding the phase boundary weight fractions w_i (between the isotropic and biphasic regions) = 0.230 and w_a (between the biphasic and liquid-crystal regions) = 0.259, respectively. This linearity of the plot is as expected for this sample of narrow molecular-weight distribution. The values of w_i and w_a for the samples used in this study are listed in *Table 1*. It can be seen that the w_i and w_a values for sample K-2 are smaller than those for sample Z-2 but larger than those for sample Z-20. Indeed, as seen in *Figure 2*, these data are consistent with our previous data for the same polymer–solvent system[14]. It is noted that both w_i and w_a exhibit rapid decreases with increasing M_w up to M_w of about 4×10^4 but become almost constant at higher molecular weights, and that the ratio w_a/w_i is smaller than 1.2 at all molecular weights.

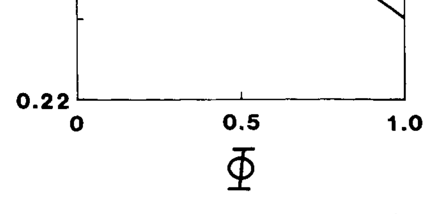

Figure 1 Plot of w vs. Φ for the system PHIC K-2+toluene at 25°C

Table 1 Phase separation results for the binary systems of PHIC and toluene at 25°C

Sample	$M_w/10^4$	w_i	ϕ_i	w_a	ϕ_a
Z-2	2.09	0.298	0.265	0.322	0.288
K-2	6.80	0.230	0.203	0.259	0.229
Z-20	24.4	0.204	0.179	0.225	0.198

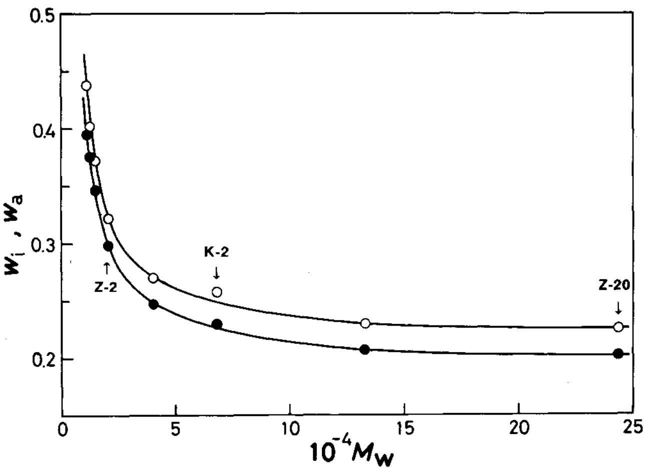

Figure 2 Molecular-weight dependence of the phase boundary concentrations w_i and w_a for PHIC in toluene at 25°C

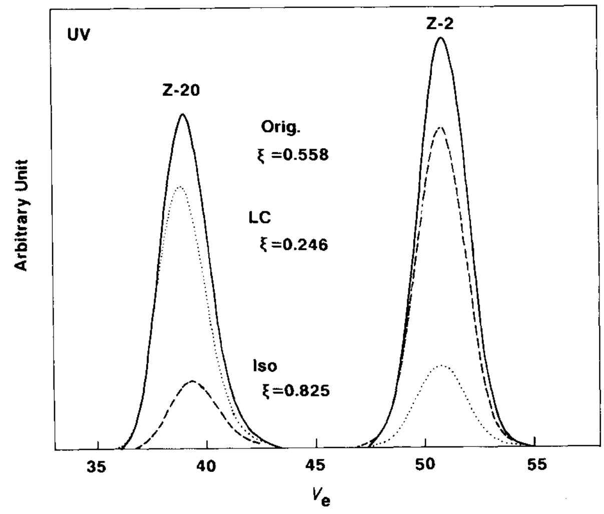

Figure 3 G.p.c. analysis of phase separation in Z-2+Z-20+toluene solution with $w=0.2679$ and $\xi=0.558$: full curve, original solution; broken curve, isotropic phase ($\xi=0.825$); dotted curve, liquid-crystal phase ($\xi=0.246$)

Ternary phase diagrams

Figure 3 illustrates g.p.c. chromatograms of the polymers in the two phases separated from a solution of PHIC Z-2+Z-20 with $w=0.2679$ and ξ (the weight fraction of the lower-molecular-weight sample in the polymer mixture) = 0.558, where the chromatogram of the whole polymer is included for comparison. It can be seen that the two peaks corresponding to the two polymer components are well separated from each other. Thus, the ξ value in each solution can be estimated accurately from the area ratio of the two peaks. The shape of each peak for the polymer recovered from the phase-separated mixtures is almost the same as that for the original polymer, although the peak position differs slightly.

It can be seen in *Figure 3* that the solution with $\xi=0.558$ separated into an isotropic phase rich in the lower-molecular-weight component Z-2 ($\xi_i=0.825$) and a liquid-crystal phase rich in the higher-molecular-weight component Z-20 ($\xi_a = 0.246$); the subscripts i and a refer to the quantities associated with the isotropic and liquid-crystal phases, respectively. This fractionation according to molecular weight was observed for all solutions of mixtures Z-2+Z-20 and K-2+Z-20, as also observed for ternary solutions of aqueous schizophyllan[3,4]. All the numerical data for the ternary systems of PHIC and toluene are summarized in *Table 2*.

The triangular phase diagram for the system Z-2+Z-20+toluene at 25°C is shown in *Figure 4*, with the total polymer weight fraction w and ξ as the composition variables. Here, the original mixtures indicated by crosses separated into the isotropic and liquid-crystal solutions indicated by triangles connected by a tie line; the thick full curves connecting the triangles represent the phase boundaries or binodals. The two pairs of full circles at the ends of the binodals represent the phase boundaries for the respective binary solutions. The binodals are curved and the phase gap, namely the region in which phase separation occurs, is slightly bulged. *Figure 5* shows the phase diagram for the system K-2+Z-20+toluene with smaller molecular-weight ratio of polymer components. The binodals of this system are almost straight and the phase gap is narrower than that for the system Z-2+Z-20+toluene.

Table 2 Phase separation data for the ternary systems of PHIC and toluene at 25°C

Original solution			Isotropic phase			Liquid-crystal phase		
w	ξ	Φ	w_i	ϕ_i	ξ_i	w_a	ϕ_a	ξ_a
K-2+Z-20+toluene								
0.2184	0.267	0.856	0.211	0.185	0.389	0.221	0.194	0.248
0.2233	0.361	0.610	0.217	0.191	0.424	0.238	0.210	0.352
0.2257	0.501	0.651	0.223	0.196	0.657	0.229	0.202	0.435
0.2318	0.604	0.558	0.240	0.212	0.804	0.247	0.218	0.476
0.2446	0.752	0.439	0.232	0.204	0.971	0.251	0.222	0.696
0.2427	0.897	0.261	0.236	0.208	0.928	0.250	0.221	0.881
0.2396	0.950	0.745	0.222	0.195	1.00	0.258	0.228	0.919
Z-2+Z-20+toluene								
0.2402	0.239	0.456	0.234	0.206	0.348	0.261	0.231	0.174
0.2596	0.417	0.470	0.246	0.217	0.666	0.296	0.263	0.190
0.2679	0.558	0.557	0.272	0.241	0.825	0.300	0.267	0.246
0.3102	0.896	0.468	0.300	0.267	1.00	0.333	0.298	0.801
0.3171	0.771	0.459	0.292	0.260	1.00	0.340	0.305	0.598
0.3181	0.951	0.537	0.307	0.274	1.00	0.339	0.304	0.891

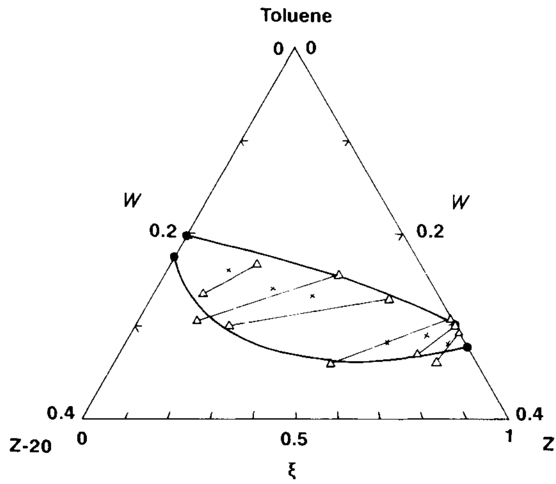

Figure 4 Triangular phase diagram for the system Z-2+Z-20+toluene at 25°C: crosses, original solutions; triangles, phase-separated solutions; thin full lines, tie lines; full circles, phase boundaries for the corresponding binary systems

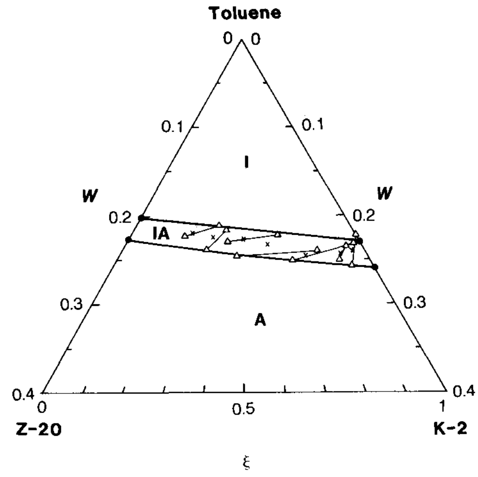

Figure 5 Ternary phase diagram for the system K-2+Z-20+toluene at 25°C. Symbols are the same as in *Figure 4*

It is noted that both phase diagrams in *Figures 4* and *5* have neither a triphase region (IAA) nor a two-liquid-crystal-phase region (AA). These phase diagrams are in contrast with the phase diagrams of the system schizophyllan J-22+T-3+water[16] and schizophyllan U-110+T-3+water[3,4] with molecular-weight ratios 7.2 and 12.2, respectively, in which both regions exist. Note that the molecular-weight ratio is as large as 12 for the PHIC Z-2+Z-20+toluene system. Thus, the existence of regions IAA and AA is not necessarily due to a large molecular-weight ratio between the polymer components but rather it is due to a relatively large difference in phase boundary concentration between the constituent binary systems; the difference is 1.5 for the PHIC system but 2.3 and 2.7 for the schizophyllan systems.

DISCUSSION

Theoretical

Odijk[15] has extended the Khokhlov–Semenov theory[11,12] to ternary systems containing two semiflexible polymers with different lengths (KSO theory). For the ternary system consisting of n_1 shorter wormlike cylinders with length L_1 and diameter d (component 1) and n_2 longer wormlike cylinders with length L_2 and diameter d (component 2), the Helmholtz free energy ΔF can be written using the second virial approximation as:

$$\begin{aligned}\Delta F/(n_1+n_2)k_BT = {} & \text{constant} + \ln c' + (1-x)\ln(1-x) \\ & + x\ln x + (1-x)\sigma_1 + x\sigma_2 + c'[(1-x)^2 b_{11}\rho_{11} \\ & + 2x(1-x)b_{12}\rho_{12} + x^2 b_{22}\rho_{22}] \qquad (1)\end{aligned}$$

where

$$b_{jk} = (\pi/4)L_j L_k d$$

$$x = n_2/(n_1+n_2)$$

and c' is the number density of total polymer, σ_j is the orientational and conformational entropy loss for the semiflexible polymer due to liquid-crystal formation, and $b_{jk}\rho_{jk}$ is the orientation-dependent excluded volume between polymers j and k. Explicit expressions for σ_j and ρ_{jk} are obtained by assuming the form of the orientational distribution function f_j. While Khokhlov and Semenov used the Onsager trial function for f_j, Odijk applied the Gaussian trial function:

$$f_j = (\alpha_j/4\pi)\exp(-\alpha_j\theta^2/2) \qquad (2)$$

where θ is the angle between the director and a segment of polymer j and α_j is a parameter which represents the degree of orientation. The latter trial function is a cruder approximation than the former but produces simpler expressions for σ_j and ρ_{jk} which make phase diagram calculation possible:

$$\sigma_j = \ln\alpha_j + \alpha_j N_j/3 + \tfrac{5}{12}\ln[\cosh(\tfrac{2}{5}\alpha_j N_j)] - \tfrac{19}{12}\ln 2 \qquad (3)$$

$$\rho_{jk} = 4(\alpha_j + \alpha_k)^{1/2}/(2\pi\alpha_j\alpha_k)^{1/2} \qquad (4)$$

The isotropic–liquid crystal phase equilibrium conditions consist of three coexistence equations for osmotic pressure Π and chemical potential μ_j of component j:

$$\Pi_{\mathrm{i}} = \Pi_{\mathrm{a}} \qquad (5a)$$

$$\mu_{1,\mathrm{i}} = \mu_{1,\mathrm{a}} \qquad (5b)$$

$$\mu_{2,\mathrm{i}} = \mu_{2,\mathrm{a}} \qquad (5c)$$

and two stabilizing conditions of the liquid-crystal phase:

$$(\partial\Delta F/\partial\alpha_1) = 0 \qquad (6a)$$

$$(\partial\Delta F/\partial\alpha_2) = 0 \qquad (6b)$$

where the subscripts i and a represent the quantities associated with the isotropic and anisotropic phases, respectively. The expressions for Π and μ_j can be obtained by differentiating ΔF in equation (1).

The theoretical phase diagram is obtained by numerically solving five simultaneous equations (5a)–(6b) for the six unknowns c_{i}', c_{a}', x_{i}, x_{a}, α_1 and α_2, among which x_{i} or x_{a} can be specified arbitrarily. Odijk[15] solved equations (5a), (6a) and (6b) only for α_1, α_2 and c_{a}' using the experimental values of c_{i}', x_{i} and x_{a} for our ternary systems of schizophyllan and water[3,4], and compared calculated and experimental values of c_{a}'. However, equations (5b) and (5c) must also hold at equilibrium, which has not been checked in Odijk's analysis. Therefore, his comparison between the KSO theory and experiment was not satisfactory. In what follows, we solve all the equations (5a)–(6b) numerically to make direct comparison between the theory and our experiment.

Comparison between the KSO theory and experiment

The calculation of the phase diagram from KSO theory needs the diameter d, the contour length L and the number of Kuhn statistical segments N. The value of d was estimated from the partial specific volume to be 1.25 nm for PHIC in toluene[14] and 1.67 nm for schizophyllan in water[7,8]. The values of L and N were calculated from the weight-average molecular weight M_{w}, the molecular weight per unit contour length M_{L} and the persistence length q: $M_{\mathrm{L}} = 740\,\mathrm{nm}^{-1}$ and $q = 37$ nm for PHIC[17]; $M_{\mathrm{L}} = 2150\,\mathrm{nm}^{-1}$ and $q = 200$ nm for schizophyllan[6].

As in the previous studies[3,4], the volume fraction ϕ of total polymer and ξ are used as composition variables in the comparison between theory and experiment. The theoretical values of ϕ were calculated from the relation:

$$\phi = (\pi/4)d^2[L_1(1-x) + L_2 x]c' \qquad (7)$$

while the experimental values were found from

$$\phi = v_{\mathrm{p}}w/[v_{\mathrm{p}}w + v_0(1-w)]$$

where v_{p} and v_0 are the partial specific volume of polymer and the solvent specific volume, respectively. The experimental values of ϕ are listed in *Tables 1* and *2*.

Figure 6 shows the KSO theoretical phase diagrams for the two systems of bidisperse PHIC and toluene. In the figures, the thick full curves are binodals and thin full lines are tie lines. The areas I, A and IA are the isotropic,

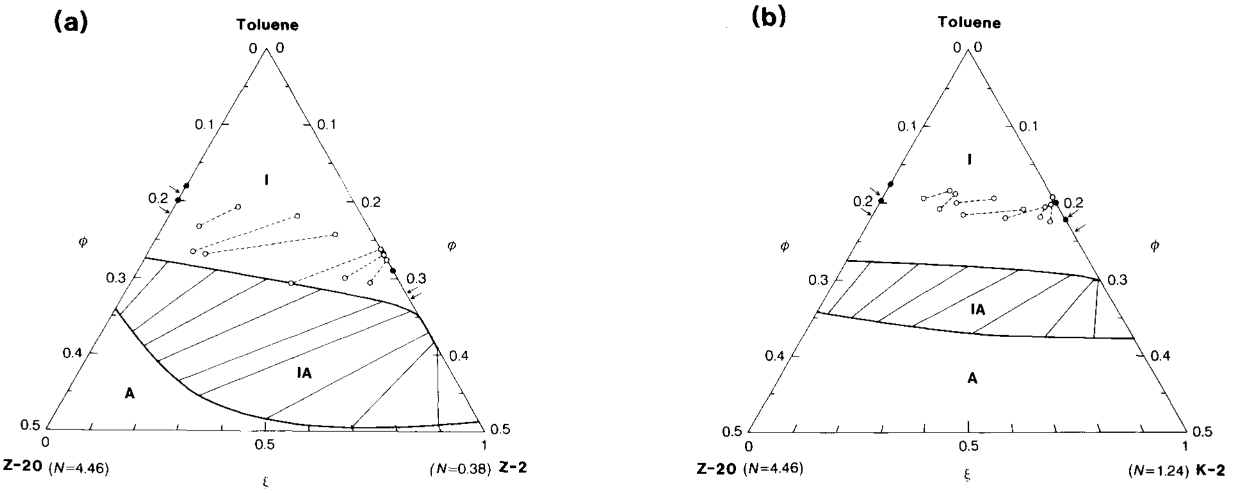

Figure 6 Ternary phase diagrams calculated from the KSO theory for the PHIC+toluene systems (a) Z-2+Z-20+toluene and (b) K-2+Z-20+toluene: thick full curves, theoretical binodals; thin full lines, theoretical tie lines; experimental data are shown by circles (phase boundaries) and broken lines (tie lines). The arrows indicate the phase boundaries calculated from the Khokhlov–Semenov theory for the corresponding binary systems

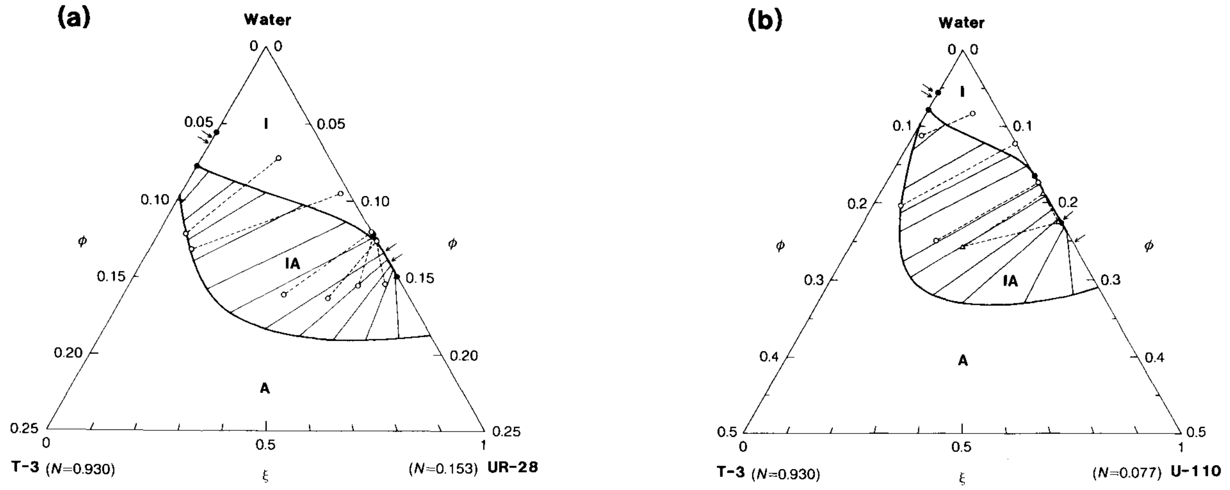

Figure 7 KSO theoretical phase diagrams for aqueous schizophyllan systems (a) UR-28 + T-3 + water and (b) U-110 + T-3 + water: same symbols as in *Figure 6* (triangles in (b) show the compositions of the three coexisting phases)

liquid-crystal and coexistence regions, respectively. For both systems, the shape of the binodals and the inclination of the tie lines bear a close resemblance to the experimental results shown by circles and broken lines. These theoretical phase diagrams have no IAA (one isotropic and two liquid-crystal phases) and AA (two liquid-crystal phases) regions, being consistent with the experimental ones. However, for either system, the theoretical binodals appear at higher ϕ than the experimental results.

Figure 7a compares the experimental results for schizophyllan UR-28 + T-3 + water[4] with the KSO theory. As for the systems of PHIC and toluene, the theory successfully predicts the isotropic–liquid crystal phase coexistence, except that the coexistence region shifts slightly to higher ϕ. For the system of schizophyllan U-110 + T-3 + water[4], the theoretical and experimental phase diagrams are compared in *Figure 7b*. Again, the KSO theory agrees with the experiment fairly well with respect to the coexistence of isotropic and liquid-crystal phases. However, it fails to predict the existence of regions IAA and AA. For the system of schizophyllan J-22 + T-3 + water[16] also, IAA and AA phase separations were observed experimentally, but were not predicted from KSO theory. In general, the three-phase separation is sensitive to the functional form of the free energy of the system. The failure of KSO theory may be due mainly to the neglect of the third and higher virial terms in the free energy as in equation (1) and the Gaussian approximation.

Previously[3,4], we compared our experimental results for aqueous schizophyllan with Abe and Flory's theory[1] for bidisperse rods. The theoretical phase diagrams had much larger multiphase regions than the experimental ones. A similar difference between Abe and Flory's theory and experiment was found for the PHIC–toluene systems*. In a comparison of *Figure 7* with figures 7 and 8 in ref. 4, it can be seen that the phase diagrams from the KSO theory are improved much more than those from Abe and Flory's theory. This leads us to conclude that chain flexibility is the primary reason for the disagreement between Abe–Flory theory and experiment, and it is important in phase equilibrium in the ternary system of bidisperse semiflexible polymers as well as in binary semiflexible polymer solution[14].

CONCLUDING REMARKS

We have compared our experimental ternary phase diagrams of PHIC–toluene and schizophyllan–water with the KSO theory for bidisperse semiflexible polymers. The KSO theory gives much better agreement with experiment than Abe and Flory's theory. However, some problems still remain in KSO theory:

(1) The isotropic–liquid crystal phase coexistence region deviates towards higher ϕ.

(2) The IAA three-phase separation and AA phase coexistence were not predicted.

The Gaussian orientational distribution function (equation (2)) may be responsible for the former discrepancy, because this discrepancy already appears in the binary system for $\xi = 0$ or 1, where the Onsager trial function produces phase boundary concentrations closer to the experimental results[14] (see the arrows in *Figures 6* and *7*). The application of the Onsager trial function to the KSO theory has not been achieved yet. In addition to the use of the correct distribution function, the prediction of three-phase separation may need the consideration of higher virial terms and the chain flexibility effect on the excluded volume for semiflexible polymers.

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* The Onsager theory for bidisperse rods[13] also predicts phase diagrams with large multiphase regions for our systems of PHIC and schizophyllan. Some of them have ϕ_a which exceeds unity. This unrealistic prediction is due to the second virial approximation

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