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Statistical Thermodynamics of Mixtures of Semirigid Macromolecules: Chains with Rodlike Sequences at Fixed Locations

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ABSTRACT: Semirigid macromolecules consisting of one or more rigid, rodlike sequences of units in combination with flexible (random coil) units are treated according to the adaptation of the lattice model to a system of rods. The lengths and locations of the rigid sequences within each macromolecule are considered to be fixed by its structure. They are separated by various specified numbers of random coiled units. Polydispersity is taken into account. General expressions are derived for the chemical potentials, and biphasic equilibria between nematic and isotropic phases are investigated. The presence of a very few random coiled units increases the disorder in the anisotropic phase, narrows the biphasic gap, and suppresses fractionation of species differing in length in polydisperse systems. The introduction of internal points of flexure, even in absence of intervening random units, produces similar effects to a degree that depends markedly on the locations of the points of flexure.

Introduction

The lattice theory[1-3] of binary mixtures of a rigid, rodlike solute with a small-molecule solvent leads to predictions in semiquantitative agreement with numerous observations. In particular, the predicted minimum solute concentration necessary for the separation of a stable anisotropic phase in exothermal and in nearly athermal mixtures is in good accord with experiments on poly(γ-benzyl L-glutamate) in *m*-cresol[4,5] and in dimethylformamide,[6] on poly(*p*-benzamide) in *N*,*N*-dimethylacetamide,[7] and on poly(hexyl isocyanate) in tetrachloroethane.[8] In fact, theory and experiment may be in better agreement than was first indicated, when the onset of phase separation was identified erroneously with the sharp drop in viscosity that occurs upon increasing the solute concentration. Recent studies[5,8,9] demonstrate that incipient phase separation occurs at a lower concentration than that at which the viscosity is observed to decrease. Revision of the experimental analysis gives promise of improved agreement between theory and experiment.[9] Other general features of the phase diagrams for α-helical polypeptides observed in various solvents, ranging from good to marginally poor ones, are in qualitative accord with theory.[10-12]

Departures from theory exhibited by polymers of high molecular weight in the systems mentioned are attributable to limited degrees of flexibility, which introduce deviations from the perfect rigidity assumed in the theory. Partial flexibility may arise either from the cumulative effects of small deviations from strict rectilinearity at each unit of the chain or from the presence of occasional structural or conformational irregularities that introduce abrupt changes in the direction of the chain backbone. The *p*-phenylene polyamides appear to be illustrative of the former type of partial flexibility.[13,14] We consider here departures from complete rigidity of the second kind. In particular, we treat semirigid chains which contain inherently flexible units, or sequences of such units, at certain locations along the otherwise rigid chain. Thus, the points or regions of flexibility are predetermined by the structure. The alternative case of mobile equilibrium between rodlike and irregular conformations, with every unit potentially eligible for either of the two forms, will be treated in a subsequent paper.[15]

A molecule of the kind here considered is shown schematically in Figure 1a. It comprises three sequences of units committed to the rigid, rodlike form. In general, these sequences are separated by sections of randomly coiled units of variable length. The limiting case in which the length of an intervening section of random units vanishes is illustrated by one of the junctions shown in the figure. The directions of the several rodlike sequences are assumed to be mutually uncorrelated by the intramolecular connections. They are indicated in Figure 1a, however, to be correlated with the domain axis of a nematic phase. Examples of semirigid chains of this kind are afforded by certain copolymers. Copolypeptides that consist of long sequences of strongly helicogenic residues separated by blocks of non-helix-forming residues, such as glycine or proline, are illustrative.

Previously we have shown[16] that a system of identical rods joined by flexible connections should exhibit nematic-isotropic phase equilibria that very nearly coincide with the equilibria for disconnected rods of the same length. Ternary systems consisting of rigid rods, random coils, and a diluent also were investigated on the basis of the lattice model.[17] It was deduced that the random coiled component should exert a marked effect on the biphasic equilibrium. This component was predicted to be virtually excluded from the nematic phase, and the rodlike component was preferentially rejected by the isotropic phase. These predictions have been confirmed by experiments reported by Aharoni[8,18] on polyisocyanates. The present investigation concerns solutes that incorporate both features in the same molecule, i.e., rigid, rodlike sequences whose orientations are mutually independent and intervening sequences of random coiled units of variable length. The effects of these latter units on biphasic equilibria are the main concern of this study.

Derivation of the Configuration Partition Function

In order to meet the requirements of a lattice model, a segment is defined as that portion of the chain having a length equal to its diameter. The length of a solute molecule is denoted by the number x of segments it contains. For simplicity, the solvent molecule is assumed to be quasi-spherical and equal in size to one segment. Hence, each cell of the cubic lattice may be occupied alternatively by a molecule of solvent or by a solute segment. Further, we adopt the device of representing the rigid sequences in the nematic phase by sub-sequences (previously[1,2]

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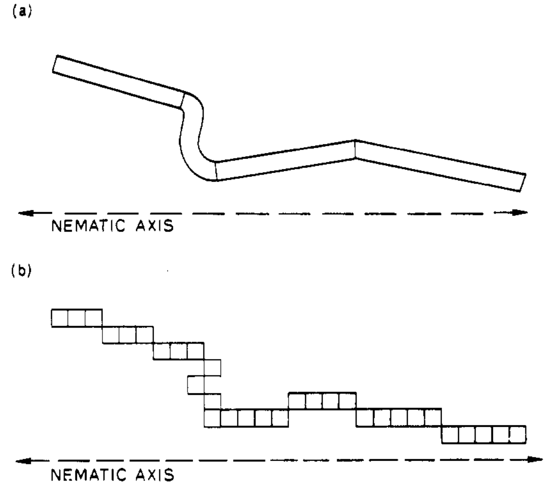

Figure 1. (a) Schematic representation of a semirigid chain containing three rodlike portions and one flexible section. (b) Representation of the semirigid chain on a lattice; the sub-sequences are heavy lined.

termed submolecules) of segments parallel to the preferred axis, as shown in Figure 1b. The preferred axis, X in the figure, is taken parallel to a principal axis of the lattice.

The partition function Z_M for the mixture is derived by assemblage of factors as follows:

$$Z_M = Z_{\text{comb}} Z_{\text{orient}} \exp(-\chi v_s \sum_x x n_x) \tag{1}$$

where Z_{comb} is the combinatory or "steric" factor, Z_{orient} takes account of the orientation of the rodlike sequences, and the third factor introduces the exchange free energy of interaction between solvent and solute; v_s is the volume fraction of solvent, n_x is the number of solute molecules consisting of x segments, and χ is the familiar interaction parameter.

The primary expression for the combinatory factor is

$$Z_{\text{comb}} = \prod_{j=1}^{n_p} \nu_j (z_c)^{x_j^c} / \prod n_x! \qquad (2)^{19}$$

where ν_j is the expected number of situations accessible to the jth solute molecule added to the lattice, n_p is the total number of solute molecules, and, borrowing from the notation of helix–coil theory for polypeptides and polynucleotides, z_c is the internal configuration partitition function for a coil segment relative to $z_h = 1$ for a rodlike segment; x_j^c and x_j^h are the numbers of random coil and rigid segments, respectively, the total number of segments in this molecule being

$$x_j = x_j^c + x_j^h \tag{3}$$

Implementation of eq 2 depends on derivation of an expression for ν_j. Following the procedure used previously,[1-3] we obtain at once

$$\nu_j = (n_0 - \sum_1^{j-1} x_i) \times \left[\frac{n_0 - \sum_1^{j-1} x_i}{n_0}\right]^{x_j^c + y_j - 1} \left[\frac{n_0 - \sum_1^{j-1} x_i}{n_0 - \sum_1^{j-1}(x_i^h - y_i)}\right]^{x_j^h - y_j} \tag{4}$$

where n_0 is the total number of sites in the lattice, i.e.

$$n_0 = n_s + \sum_{i=1}^{n_p} x_i = n_s + \sum x n_x \tag{5}$$

n_s being the sub-sequences of solvent molecules; y_i is the number of sub-sequences required to render the rodlike sections of molecule i conformable to the cubic lattice, given their inclinations to the preferred axis (see Figure 1b). The quantity y_i serves also as a measure of disorientation of molecule i. The first factor on the right-hand side of eq 4 is the number of vacant lattice sites to which the first segment of chain j may be assigned. The following factor in square brackets expresses the a priori expectation of vacancy of the site required for a coil segment or for the first segment of a rigid sub-sequence. The last factor in brackets is the conditional expectation of vacancy at the site required for a succeeding segment of a sub-sequence, given that the preceding one is vacant; it is expressed by the number fraction of vacancies,[1-3] i.e., the ratio of vacancies to the sum of vacancies and sub-sequences.

Replacement of the factors raised to powers in eq 4 by ratios of factorials and substitution in eq 2 yields

$$Z_{\text{comb}} = \frac{[n_0 - \sum_{i=1}^{n_p}(x_i^h - y_i)]!(z_c)^{\sum_i x_i^c}}{n_s! \prod_x n_x! n_0^{\sum_i (x_i^c + y_i - 1)}} \tag{6}$$

The summations may be reduced through use of the relations

$$\begin{gathered} \sum_1^{n_p} x_i^h = \sum_x \sum_\eta \eta \gamma_{x,\eta} = \theta_h \sum x n_x = \theta_h \bar{x} n_p \\ \sum_1^{n_p} x_i^c = (1 - \theta_h) \bar{x} n_p \\ \sum_1^{n_p} y_i = \sum_\eta y_\eta \sum_x n_x \gamma_{x,\eta} = \theta_h \bar{x} n_p (\bar{y}/\bar{\eta}) \end{gathered} \tag{7}$$

where θ_h is the fraction of rigid segments in all solute molecules, $\bar{x}$ is the number-average chain length, $\gamma_{x,\eta}$ is the number of rigid sequences η segments in length in a molecule of size x and $\sum_x n_x \gamma_{x,\eta}$ is the total number of sequences of this length or axial ratio, y_η is the average disorientation for such sequences, y being assumed to depend only on the length η of a sequence and not on the size x of the molecule in which it is situated,[15] $\bar{\eta}$ is the mean length of a rodlike sequence averaged over all molecules, and $\bar{y}$ is the average disorientation for all sequences. Substitution of eq 5 and 7 in eq 6 yields

$$Z_{\text{comb}} = \frac{\{n_s + \bar{x} n_p [1 - \theta_h (1 - \bar{y}/\bar{\eta})]\}!(z_c)^{\bar{x} n_p (1 - \theta_h)}}{n_s! (\prod n_x!) n_0^{\bar{x} n_p [1 - \bar{x}^{-1} - \theta_h (1 - \bar{y}/\bar{\eta})]}} \tag{8}$$

Under the assumption that the orientation distribution for rigid sequences depends only on their length η, we let

$$Z_{\text{orient}} = \prod_\eta \prod_y [\omega_{\eta,y} \sum_x n_x \gamma_{x\eta} / \sum_x n_x \gamma_{x,\eta,y}]^{\sum_x n_x \gamma_{x,\eta,y}} \tag{9}$$

where $\gamma_{x,\eta,y}$ is the expected number of rodlike sequences of length η and disorientation y in a molecule of size x and $\omega_{\eta,y}$ is the a priori probability of this disorientation; $\omega_{\eta,y}$ reflects the range of solid angle associated with y for the designated value of η. Exact treatment according to eq 9 is possible but tedious.[3] In its stead we use the approximate expression

$$Z_{\text{orient}} = \prod_\eta (y_\eta^2 \exp C)^{\sum_x n_x \gamma_{x,\eta}} \tag{10}$$

In the limit of small average disorientations, eq 9 reduces to eq 10, with C given by[3]

$$C = 2 \ln (\pi e/8) = 0.131 \tag{11}$$

The error entailed by this "asymptotic" approximation[3] is generally small. For high degrees of disorder, however, the "1956" approximation[1] obtained by taking $C = 0$ in eq 10 is preferable.

Free Energy of Mixing and Equilibrium Disorder

Substitution of eq 8 and 10 in eq 1 and introduction of Stirling's approximation for the factorials gives

$$\Delta G_{\mathrm{M}}/RT = -\ln Z_{\mathrm{M}} = n_{\mathrm{s}} \ln v_{\mathrm{s}} + \sum n_x \ln (v_x/x) + (n_{\mathrm{s}} + \bar{x}n_{\mathrm{p}})[(1 - 1/\bar{x})v_{\mathrm{p}} - (1 - Q) \ln (1 - Q) - Q - v_{\mathrm{c}} \ln z_{\mathrm{c}} + \chi v_{\mathrm{s}} v_{\mathrm{p}}] - \sum_x \sum_\eta n_x \gamma_{x,\eta} (\ln y_\eta{}^2 + C) \quad (12)$$

for the reduced free energy of mixing, where $v_{\mathrm{h}} = \theta_{\mathrm{h}} v_{\mathrm{p}}$ and $v_{\mathrm{c}} = (1 - \theta_{\mathrm{h}})v_{\mathrm{p}}$ are the volume fractions of rigid and random coiled segments, respectively, $v_{\mathrm{p}} = v_{\mathrm{c}} + v_{\mathrm{h}}$ is the volume fraction of solute in the mixture, and

$$Q = v_{\mathrm{h}}(1 - \bar{y}/\bar{\eta}) \quad (13)$$

$$Q = [\sum_\eta \sum_x n_x \gamma_{x,\eta}(\eta - y_\eta)]/(n_{\mathrm{s}} + \bar{x}n_{\mathrm{p}}) \quad (13')$$

Differentiating eq 12 with respect to y_η and equating to zero, one obtains

$$\exp(-2/y_\eta) = 1 - v_{\mathrm{h}}(1 - \bar{y}/\bar{\eta}) = 1 - Q \quad (14)$$

which corresponds to the condition for equilibrium disorder previously found[1-3] for a system of independent rods. The lower of the two solutions to eq 14, if real solutions exist, is the physically significant one that minimizes the free energy. The equilibrium value y_η thus deduced is independent of η; hence we drop the subscript and let $y_\eta = y$ provided that $\eta > y$. For sequences $\eta \leq y$, the free energy decreases monotonically with y_η to the limit $y_\eta = \eta$, and solutions to eq 14 do not exist. For such sequences the disorder parameter reaches its upper limit[3] $y = \eta$. They are therefore unoriented.

Adopting the procedure used previously,[2,20] we distinguish unoriented sequences in the latter category from aligned ones (designated by the superscript a) having lengths η exceeding y. Then

$$\bar{y} = [\sum_x \sum_{\eta \leq y} \eta n_x \gamma_{x,\eta} + y \sum_x \sum_{\eta > y} n_x \gamma_{x,\eta}] / \sum_x \sum_\eta n_x \gamma_{x,\eta} = (v_{\mathrm{h}}{}^{\mathrm{r}}/v_{\mathrm{h}})\bar{\eta} + (y/\bar{\eta}^{\mathrm{a}})(v_{\mathrm{h}}{}^{\mathrm{a}}/v_{\mathrm{h}})\bar{\eta} \quad (15)$$

where $v_{\mathrm{h}}{}^{\mathrm{r}}$ and $v_{\mathrm{h}}{}^{\mathrm{a}}$ are the volume fractions of rigid sequences that are oriented at random ($\eta \leq y$) and aligned ($\eta > y$), respectively; $\bar{\eta}^{\mathrm{a}}$ is the average length of aligned sequences, i.e.

$$\bar{\eta}^{\mathrm{a}} = \sum_x \sum_{\eta > y} \eta n_x \gamma_{x,\eta} / \sum_x \sum_{\eta > y} n_x \gamma_{x,\eta}$$

Substitution of eq 15 in eq 13 yields

$$Q = v_{\mathrm{h}}{}^{\mathrm{a}}(1 - y/\bar{\eta}^{\mathrm{a}}) \quad (16)$$

$$Q = (n_{\mathrm{s}} + \bar{x}n_{\mathrm{p}})^{-1}[\sum_x \sum_{\eta > y} n_x(\eta - y)\gamma_{x,\eta}] \quad (16')$$

Substitution of eq 16 in eq 14 and replacement of y_η by y give

$$\exp(-2/y) = 1 - v_{\mathrm{h}}{}^{\mathrm{a}}(1 - y/\bar{\eta}^{\mathrm{a}}) = 1 - Q \quad (17)$$

i.e., y is determined by the volume fraction and average length of the aligned sequences only (compare eq 12′ of ref 2).

It remains to separate the last term in eq 12 in the foregoing manner. For $\eta \leq y$ we set $y_\eta = \eta$ and $C = 0$; for $\eta > y$ we let $y_\eta = y$ and retain C as defined by eq 11. The resulting rendition of the reduced free energy can be cast in a form suitable for differentiation by substituting eq 16′ for Q and by expressing all quantities in terms of numbers of species. The result is

$$\Delta G_{\mathrm{M}}/RT = n_{\mathrm{s}} \ln n_{\mathrm{s}} + \sum n_x \ln n_x - (n_{\mathrm{s}} + \sum n_x) \ln (n_{\mathrm{s}} + \sum x n_x) + \sum (x - 1)n_x - [n_{\mathrm{s}} + \sum x n_x - \sum_x \sum_{\eta > y} (\eta - y) n_x \gamma_{x,\eta}] \times \ln \left[\frac{n_{\mathrm{s}} + \sum x n_x - \sum_x \sum_{\eta > y} (\eta - y) n_x \gamma_{x,\eta}}{n_{\mathrm{s}} + \sum x n_x} \right] - \sum_x \sum_{\eta > y} n_x \eta \gamma_{x,\eta} - \sum_x n_x (x - \sum_\eta \eta \gamma_{x,\eta}) \ln z_{\mathrm{c}} - \sum_x \sum_{\eta \leq y} n_x \ln \eta^2 \gamma_{x,\eta} + (y - \ln y^2 - C) \sum_x \sum_{\eta > y} n_x \gamma_{x,\eta} + \chi n_{\mathrm{s}} \sum x n_x / (n_{\mathrm{s}} + \sum x n_x) \quad (18)$$

Chemical Potentials and Conditions for Phase Equilibrium

The chemical potential of the solvent obtained by differentiation of eq 18, with y assumed to have its equilibrium value so that $\partial \Delta G_{\mathrm{M}}/\partial y = 0$, is

$$(\mu_{\mathrm{s}} - \mu_{\mathrm{s}}{}^\circ)/RT = \ln v_{\mathrm{s}} + (1 - 1/\bar{x})v_{\mathrm{p}} - \ln (1 - Q) - Q + \chi v_{\mathrm{p}}{}^2 \quad (19)$$

Substitution from eq 17 for the system at orientational equilibrium yields

$$(\mu_{\mathrm{s}} - \mu_{\mathrm{s}}{}^\circ)/RT = \ln (1 - v_{\mathrm{p}}) + (1 - 1/\bar{x})v_{\mathrm{p}} + 2/y - [1 - \exp(-2/y)] + \chi v_{\mathrm{p}}{}^2 \quad (19')$$

The chemical potential of the solute obtained similarly by differentiating eq 18 with respect to n_x is

$$(\mu_x - \mu_x{}^\circ)/RT = \ln (v_x/x) + (1 - 1/\bar{x})x v_{\mathrm{p}} - [x - \sum_{\eta > y} (\eta - y)\gamma_{x,\eta}] \times \ln (1 - Q) - Qx - (x - \sum_\eta \eta \gamma_{x,\eta}) \ln z_{\mathrm{c}} - \sum_{\eta \leq y} \gamma_{x,\eta} \ln \eta^2 - (\ln y^2 + C) \sum_{\eta > y} \gamma_{x,\eta} + x \chi v_{\mathrm{s}}{}^2 \quad (20)$$

Or, by substitution of eq 17

$$(\mu_x - \mu_x{}^\circ)/RT = \ln (v_x/x) + (1 - 1/\bar{x})x v_{\mathrm{p}} + 2x/y - 2\sum_{\eta > y} (\eta/y - 1)\gamma_{x,\eta} - x[1 - \exp(-2/y)] - (x - \sum_\eta \eta \gamma_{x,\eta}) \ln z_{\mathrm{c}} - \sum_{\eta \leq y} \gamma_{x,\eta} \ln \eta^2 - (\ln y^2 + C) \sum_{\eta > y} \gamma_{x,\eta} + x\chi(1 - v_{\mathrm{p}})^2 \quad (20')$$

For an isotropic mixture $y_\eta = \eta$ for all η; hence $Q = 0$, and eq 19 and 20 are replaced by

$$(\mu_{\mathrm{s}} - \mu_{\mathrm{s}}{}^\circ)/RT = \ln (1 - v_{\mathrm{p}}) + (1 - 1/\bar{x})v_{\mathrm{p}} + \chi v_{\mathrm{p}}{}^2 \quad (21)$$

and

$$(\mu_x - \mu_x{}^\circ)/RT = \ln (v_x/x) + (1 - 1/\bar{x})x v_{\mathrm{p}} - (x - \sum_\eta \eta \gamma_{x,\eta}) \ln z_{\mathrm{c}} - \sum_\eta \gamma_{x,\eta} \ln \eta^2 + x\chi(1 - v_{\mathrm{p}})^2 \quad (22)$$

We distinguish ordered and disordered phases by appending a prime to quantities for the latter phase where distinction is required. Then, by application of the coexistence condition $\mu_{\mathrm{s}}' = \mu_{\mathrm{s}}$, we obtain from eq 19′ and 21

$$\ln [(1 - v_{\mathrm{p}}')/(1 - v_{\mathrm{p}})] = (1 - 1/\bar{x})v_{\mathrm{p}} - (1 - 1/\bar{x}')v_{\mathrm{p}}' + 1 - 2/y - \exp(-2/y) + \chi v_{\mathrm{p}}{}^2 - \chi' v_{\mathrm{p}}'^2 \quad (23)$$

Similarly, from the further condition $\mu_x' = \mu_x$ and eq 20′ and 22

$$\ln (v_x'/v_x) = [(1 - 1/\bar{x})v_{\mathrm{p}} - (1 - 1/\bar{x}')v_{\mathrm{p}}' + 1 - 2/y - \exp(-2/y) + \chi(1 - v_{\mathrm{p}})^2 - \chi'(1 - v_{\mathrm{p}}')^2]x + \sum_{\eta > y} \gamma_{x,\eta}[2(\eta/y - 1) - 2 \ln (\eta/y) + C] \quad (24)$$

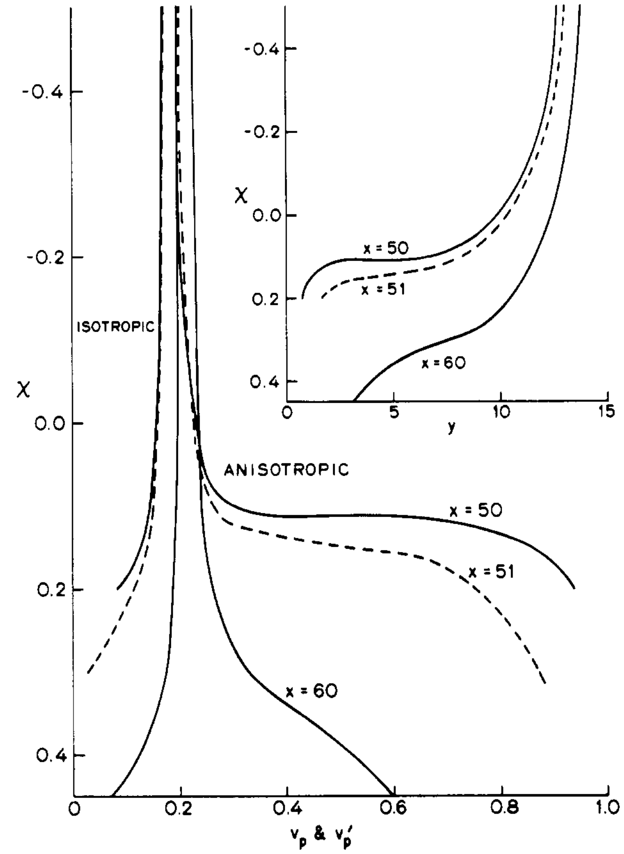

Figure 2. Phase diagrams for binary systems consisting of a solvent and a solute having a single, rodlike sequence with axial ratio 50 and appended tails of 0, 1, or 10 randomly coiled segments, as indicated. The temperature is subsumed in the interaction parameter χ plotted on the ordinate. The insert depicts the relationship between the equilibrium disorder parameter y and χ. Calculations were carried out by using the asymptotic approximation.

Equations 23 and 24, supplemented by eq 17, specify the conditions for coexistence of an isotropic and an anisotropic phase. An eq 24 is required for each solute species.

Whereas strict adherence to the model would require y for a given sequence to be an integer, the role it acquires in the theory as a parameter characterizing all sequences $\eta > y$ clearly legitimizes treatment of it as a continuously varying quantity. The number of segments x may likewise be nonintegral. Hence, the summations over η and x may appropriately be replaced by the corresponding integrals. These alterations are straightforward but are not required for the calculations that follow.

All solute species of a given size x are implicitly assumed to be identical.[19] This restriction, as it applies to the free energy and chemical potentials in a given phase, may be removed by interpretation of $\gamma_{x,\eta}$ as the *expected* number of sequences of length η in an x-mer, all species of the given size being treated collectively as a single species. This device is generally inapplicable at coexistence of separate phases inasmuch as partitioning of diverse species of the same size between phases must then occur. Such situations are avoided in the examples treated below.

Results

As examples of the utmost simplicity, we first consider monodisperse solutes comprising a single rodlike sequence or "block" of segments followed by a "tail" of randomly coiled units. Figure 2 presents phase diagrams calculated in the asymptotic approximation (i.e., with C furnished by eq 11) for three solvent–solute systems in which the solute is of this type and $x_s = 1$. The axial ratio of the rigid sequence is $\eta = 50$ in each, this block being joined to tails consisting of 0, 1, and 10 segments, respectively; i.e., $x = \eta + x^c = 50$, 51, and 60 for the three pairs of curves delineating the binodals for the two phases. The interaction parameter χ, taken to be the same in the two phases (i.e., $\chi' = \chi$), is plotted against the volume fractions v_p and v_p' of solute in the two phases.

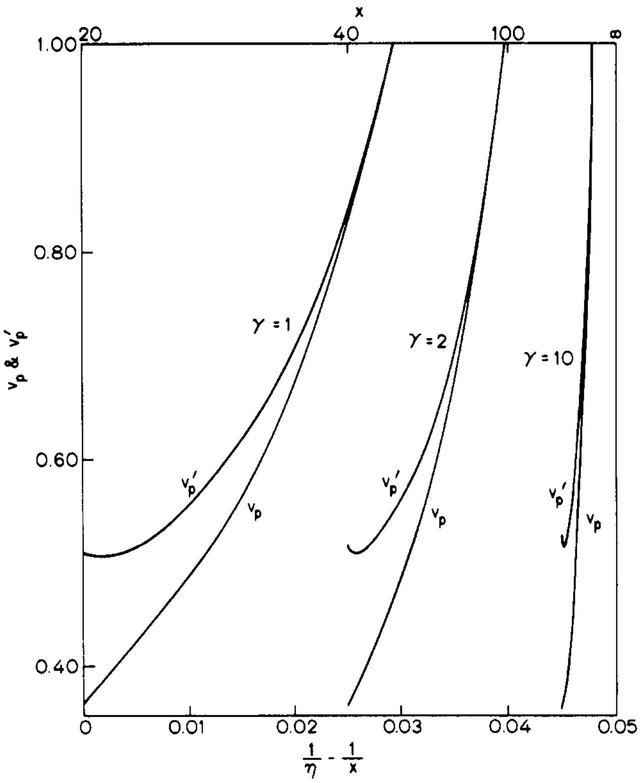

Figure 3. Values of v_p and v_p' at phase equilibrium for athermal solutions ($\chi = 0$) plotted against the function $1/\eta - 1/x$ of the total chain length x. The integer γ, which identifies conjugate pairs of composition curves, indicates the number of independent rodlike sequences of axial ratio 20 per chain. The remaining $x - 20\gamma$ segments per chain are flexible. The asymptotic approximation was employed.

The characteristic broadening of the biphasic gap that occurs[1,2,10-12,21-23] when the quality of the solvent declines into the range where χ becomes positive is markedly diminished by attachment of a tail of flexible segments to the rod, according to the calculations shown in Figure 2. As little as one such segment has a significant effect. In contrast, the influence of the tail is comparatively small in the range $\chi = \chi' < 0$. The slender corridor delineating the biphasic gap is narrowed somewhat by them and it is shifted to marginally greater concentrations.

The dependence of y on χ is displayed in the inset in Figure 2. The appendage of a sequence of flexible segments increases the disorder (y) in the anisotropic phase, the effect being greater the longer the sequence. The abrupt changes in v_p' and y that occur concomitantly with broadening of the biphasic gap, i.e., near $\chi = 0.11$ for simple rods with $x = \eta = 50$, are moderated by the presence of a tail.

Figure 3 further illustrates the effect on the biphasic equilibrium of the proportion of flexible segments in the solute molecules. The molecules considered are made up of rodlike sequences consisting of $\eta = 20$ segments, each with varying numbers of flexible segments incorporated between the rods and at the ends of the molecules. In the three cases shown in Figure 3, the number of rods in a

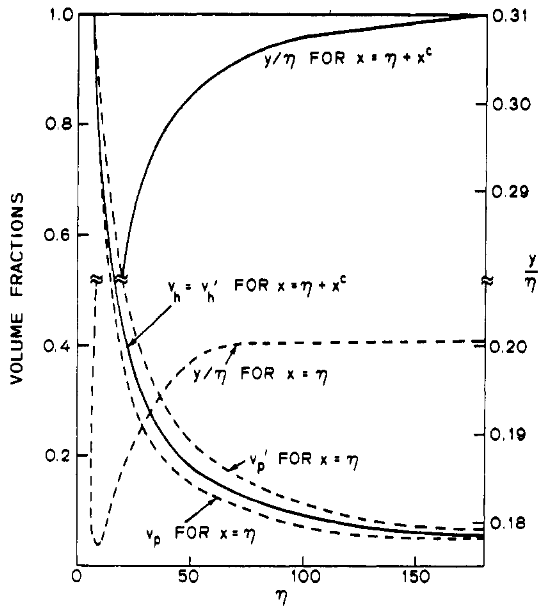

Figure 4. Values of $v_h = v_h'$ and of y calculated as functions of the axial ratio η of a single rodlike sequence when the maximum number of flexible segments permitting biphasic equilibrium is attached thereto. For comparison, the volume fractions v_p and v_p' and y/η in solvent–simple rod systems at biphasic equilibrium are shown by dashed lines. Calculations were carried out by using the asymptotic approximation.

molecule is $\gamma = 1$, 2, and 10, respectively. As the equations above show, the allocation of the flexible segments between the rods is immaterial; their total number suffices to determine the thermodynamic functions.

The volume fractions v_p and v_p' calculated for coexistence when $\chi = \chi' = 0$ are plotted in Figure 3 against $1/\eta - 1/x$, where $x = \gamma\eta + x^c$ is the total number of segments in a solute molecule. The quantity $1/\eta - 1/x$ serves as a measure of the proportion of flexible segments. Each pair of curves commences at the value of the abscissa for complete absence of flexible segments, i.e., for $x = \gamma\eta$. At this point the rodlike sequences for the molecules with $\gamma = 2$ and 10 are connected by flexible, dimensionless joints. As was shown previously,[16] the phase equilibrium for binary systems in which the solute molecules consist of flexibly connected rods depends predominantly on the axial ratio of the rodlike sequence, being little affected by the number of them so joined. This is manifested in values of v_p' and v_p that are nearly the same for the three systems at the outset for each pair, i.e., at $x = \gamma\eta$. Introduction of flexible segments decreases v_p' initially in each case. This trend is reversed when the proportion of flexible segments becomes appreciable. With further increase in the number of these segments, v_p', like v_p, rises steadily. The biphasic gap narrows and the two curves merge as they approach their common intercept at $v_p = v_p' = 1$. The location of this intercept specifies the proportion of flexible segments that can be tolerated without suppressing formation of a nematic phase when $\eta = 20$. For all values of γ examined, the ratio of flexible to rodlike segments in this limit was 1.4. The corresponding volume fraction $v_h = v_h'$ of rigid sequences is 0.417 in all cases.

In extension of these results, Figure 4 shows (descending solid curve) the volume fraction $v_h = v_h'$ of rigid sequences in molecules consisting of a single rigid sequence of length η, plotted on the abscissa, joined with the maximum number of flexible segments that can be incorporated without suppressing occurrence of a nematic phase. These calculations, like those shown in Figure 3, were carried out for $\chi = \chi' = 0$. As expected, the proportion of random segments that can be tolerated increases with η. Shown for comparison are the volume fractions v_p and v_p' (descending dashed curves) for simple rods devoid of flexible units at biphasic equilibrium when admixed with a diluent. The volume fraction of the rodlike sequence in molecules carrying random tails falls neatly between these two curves for binary systems. These curves commence at $\eta = x = 6.45$, the critical axial ratio calculated in the asymptotic approximation for "hard" rods.[3,25] In the limit of an indefinitely long rodlike sequence $\eta/x \rightarrow v_p|_{\eta=x} \approx 8/\eta$.[1,3]

Also plotted in Figure 4 are values of y/η (ascending solid curve) for the rod embedded in $x^c = x - \eta$ random segments. This disorder index at biphasic equilibrium is appreciably greater than for simple rods ($x^c = 0$) in a solvent, values of the ratio $y/\eta = y/x$ for which are shown by the lowest dashed curve.

We next consider once-broken rods consisting of $x = 40$ segments. Let the volumeless free joint occur at any point along the original rod. Values of v_p and y calculated for phase equilibrium in a binary solute–solvent system for which $\chi = \chi' = 0$ are shown in Figure 5 as a function of the location of the "break", identified by η_b, the length of the shorter of the two sequences. The disorder index y also is shown. Solid curves were calculated by using the "1956" approximation;[1,3] dashed curves represent the asymptotic approximation.[3] Calculations were not performed following the "exact" lattice theory[3] because of the excessive effort that would have been required.

Focusing on the solid curves representing the 1956 approximation in Figure 5, we observe that for breaks near the center of the molecule, i.e., for $\eta_b > 10$, neither v_p nor y depends strongly on the location of the break. As it is moved nearer to the end, however, the disorder parameter y increases rapidly until it reaches a discontinuity at $\eta_b = y = 7.3$. For smaller η_b, the disorder index exceeds the length of the shorter rods, which therefore are disordered completely.[2,20] Below the discontinuity, the effect of the longer rod dominates. This accounts for the relatively large value of y and the steep decline in v_p.

Calculations in the asymptotic approximation (dashed curves) are qualitatively similar. Inasmuch as this ap-

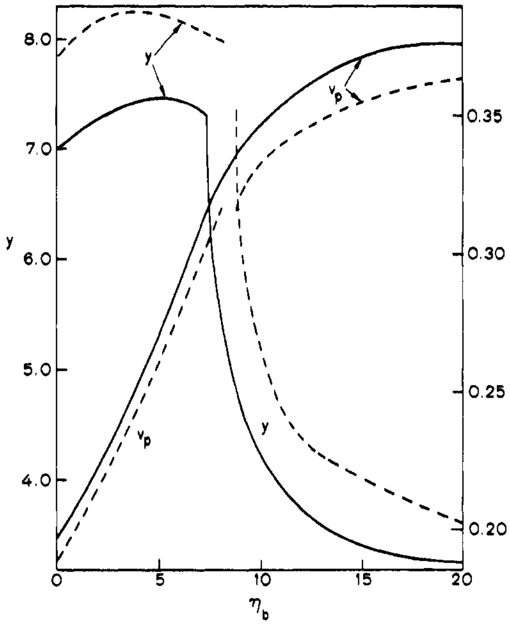

Figure 5. Equilibrium values of y and v_p for athermal solutions of a once-broken rod of total length $x = 40$ plotted against the axial ratio of the shorter of the two rodlike pieces. Solid curves were calculated by using the 1956 approximation, dashed ones by using the asymptotic approximation.

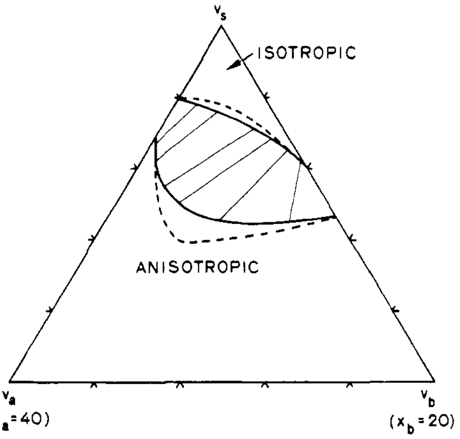

Figure 6. Phase diagram for the athermal ($\chi = 0$) system with $x_a = 40$, $\eta_a = 39$, and $x_b = \eta_b = 20$. Heavy curves represent binodals; tie lines are shown by light lines. Dashed curves represent the related system with $x_a = \eta_a = 40$ and $x_b = \eta_b = 20$.

proximation is limited to small degrees of disorder,[3] it is less satisfactory than the 1956 approximation in the vicinity of the discontinuity, where one of the component rods reaches complete disorder.

Figure 6 presents calculations for the ternary system consisting of component a with $x_a = 40$ and $\eta_a = 39$, component b with $x_b = \eta_b = 20$, and a solvent s. Binodals bounding the biphasic region are shown by heavy solid lines, tie lines by light lines. Dashed curves, taken from Figure 1 of ref 26, represent the corresponding system in which component a is a simple rod with $x_a = \eta_a = 40$. The presence of only one flexible segment has a significant effect.

Figure 7 shows the phase diagram calculated for the corresponding ternary system in which the larger solute component consists of a rodlike sequence embracing only half the length of the molecule, the remaining segments being flexible; i.e., $\eta_a = 20$ and $x_a = 40$. The biphasic gap for the binary system s–b consisting of solvent and rodlike component b with $x_b = \eta_b = 20$ is broadened by addition of component a, as is apparent from the progression of tie lines, two of which are shown (dashed) in this region of the diagram. The solvent concentrations in both coexisting phases are decreased by component a. This component is virtually excluded from the anisotropic phase ($v_a < 10^{-4}$) in a manner reminiscent of previous calculations[17] for mixtures of random coils with rodlike molecules. With further increase in the proportion of component a the volume fraction v_b in the isotropic phase decreases, reaching a value of 3×10^{-4} at the point I. This portion of the binodal for the isotropic phase has been arbitrarily displaced from the a–r axis in Figure 7a in the interest of clarity. It is interrupted at point I by the emergence of anisotropic phase A_1. Points I and A_1 actually lie very close to the compositions for the coexisting phases of the binary system s–a, the biphasic gap for this system being small. This region of the phase diagram is shown in expanded scale in Figure 7b. The portion to the left of line IA_1 represents a second biphasic region. The narrow region bounded by IA_1A_2 in Figure 7a is triphasic. The reentrant binodal terminated by A_1 and A_2, and delineating the locus of coexistence of two anisotropic phases, lies very close to the limiting tie line A_1A_2; hence, it is not shown in Figure 7.

Calculations of ternary systems consisting of two rodlike species in admixture with solvent have revealed analogous triphasic characteristics.[26] The marked effect of incorporating both rigid and flexible segments in one of the components will be apparent from comparisons of parts a and b of Figure 7 with Figure 1 of ref 26 and Figure 2 of ref 17.

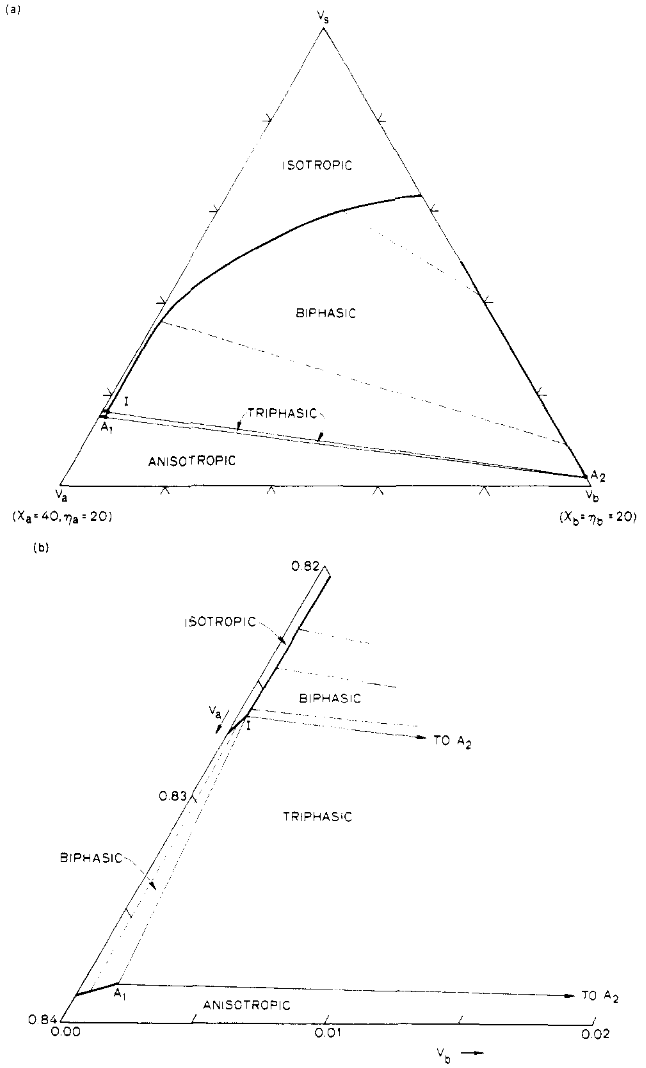

Figure 7. (a) Ternary phase diagram for the system consisting of component a comprising a rod of $\eta_a = 20$ segments joined to 20 random segments ($x_a = 40$), a simple rodlike component b with $x_b = \eta_b = 20$ segments, and a solvent ($x_s = 1$). Representative tie lines in the major biphasic region are shown by dashed lines. Solid light lines demarcate the narrow triphasic region with apices I ($v_a = 0.8263$, $v_b = 3.1 \times 10^{-4}$), A_1 ($v_a = 0.8370$, $v_b = 1.3 \times 10^{-3}$), and A_2 ($v_b = 0.9780$, $v_a = 3 \times 10^{-14}$). (b) Enlarged plot of the small biphasic region between the s–a axis and line IA_1 and the neighboring portion of the triphasic region.

Discussion

The expressions developed above for the free energy of mixing (eq 12) and the chemical potentials of solvent (eq 19 and 19′) and solute (eq 20 and 20′) are general for molecules in which the distribution of rodlike sequences is fixed. In addition to the premises of the lattice model itself,[1-3] they depend only on the assumption of independently orientable sequences. Since this latter assumption appears to be indispensable for the development of tractable equations, it is important to consider which real chain molecules comply therewith. Two qualitatively distinct types of free joints need to be distinguished. First, the hypothetical "volumeless" free joints discussed here and previously[16] constitute a useful artifice by means of which imperfect rigidity may be incorporated in the lattice treatment. Second, real points of flexure such as might be associated with flexible portions of a block copolymer constitute free joints if they are sufficiently long, albeit not volumeless ones. Thus, if rodlike blocks of segments in a copolymer are joined by sequences of at least 10–20 flexible bonds, they may be sufficiently independent to ensure applicability of the present theory. Shorter sequences (ca. 1–5 bonds) may not qualify under the terms of the present formulation. The occurrence of short, rigid sequences ($\eta \approx y$) also vitiates (see Figure 5) the treatment. With these two qualifications, the present theory for imperfectly rigid rods should be broadly applicable to real mixtures.

Calculations based on the conditions of phase equilibrium (eq 23 and 24) lead to several generalizations concerning the tendency of imperfectly rodlike chains to form anisotropic phases. First, randomly coiled units exert a pronounced influence on the properties of the conjugate phases in equilibrium. They increase the disorder in the anisotropic phase and narrow the biphasic gap. For given axial ratios of the rods, the effect of flexible segments is greater for $\chi > 0$ than for $\chi < 0$. Even though rigid sequences with $x \gtrsim 17$ can support equally long, or longer tails, the influence of even a single flexible segment is appreciable (see Figures 2 and 3). This is consistent with the result found earlier[17] that random coils are strongly excluded from the anisotropic phase. Thus, when random segments are forced into the anisotropic phase, the order is strongly perturbed. Another result of the incorporation of randomly coiled units in polydisperse systems is a marked suppression of fractionation between the isotropic and anisotropic phases, along with a contraction of the otherwise very broad biphasic gap. In the absence of randomly coiled sections, the longer rods in a polydisperse system preferentially accumulate in the anisotropic phase.[20,26] However, as the plots in Figures 6 and 7 illustrate, sufficient flexibility in the longer rods eventually reverses this trend. This suppression of fractionation and the accompanying trend toward pronounced broadening at the biphasic gap is an important attribute of randomly coiled units. It partially accounts for the failure to observe such broadening in moderately polydisperse systems that was noted previously.[20]

Second, we observe that the length of the shorter rigid sequence in the once-broken rod is important in determining the properties of the conjugate phases. When this length differs drastically from the equilibrium value of y according to eq 17, then the extent of disorder is rather insensitive to η_b. The basic assumptions underlying the treatment of the lattice model fail when $\eta_b \approx y$.

The once-broken rod is an example of a system with a dimensionless free joint. Such joints are obviously less effective than real sequences of randomly coiled units (placed in equivalent positions) in disrupting the order in an anisotropic phase. However, through their direct influence on $\bar{\eta}^a$ (see eq 17), volumeless joints can have a marked influence on the characteristics of the conjugate phases. Of course, the hypothetical volumeless joints find their utility primarily as an artifice for imitating the presence of small, random deviations from perfect rodlike rigidity. Hence, their distribution throughout the chain is of primary importance. This distribution may be properly treated as "fixed" for a homopolymeric chain in which each bond is equally subject to small, random fluctuations in direction. The distribution will be mobile (in the sense that not all chains in an ensemble will have identical points of flexure) for a polymer in which each unit can occur in either of two states, viz., rigid or random, each populated as required for equilibrium. For the former case, the properties of the system are dominated by the fixed length η of the rodlike sequence, as previous studies[16] and the results presented here clearly show. The case of mobile interconversion between rigid and flexible sequences will be treated in a later paper.[15]

As a final comment on the proper application of the present theory, we note that the anisotropic phase has been presumed to be homogeneous and nematic. To an excellent approximation cholesteric mesophases may also be included. However, smectic mesophases and phases with local clustering of rodlike and segregated randomly coiled sequences have not been considered. These types of order are not typical of binary systems (with the notable exception of amphiphilic solutes such as soaps). They are more often associated with neat fluids or cast films. The present theory could be elaborated by inclusion of interfacial free energy terms and/or correlations between the position and direction of nonrigid sequences in order to describe such systems. This is a topic inviting future study.

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