and for $x_2 = 20$ at 3.41×10^{-5}; for $x_2 = 100$ it is vanishingly small. These intercepts v_3 are shown as a function of x_2 by the solid curves in Figure 6 representing the binary systems 2,3 that occur when $v_1 = 0$. The upper solid curve has been calculated for $x_3 = \infty$ and the lower one for $x_3 = x_2$. The long dashed curve, included for comparison, represents the limiting case $x_3 = 1$ in which the second component is monomeric. Alternatively, this curve may be taken to represent the binary system 1,2 with component 1 designated as component 3. Each of these curves commences on the abscissa at the common point $x_2 = 6.70183$ which is the critical axis ratio for a system of one component.[3]

Comparison of the three curves for $x_3 = 1$, $x_3 = x_2$, and $x_3 = \infty$ in Figure 6 demonstrates the marked effect of chain length of the random coil component in expelling the rodlike species from the isotropic phase. At $x_2 = 10$ the respective volume fractions $v_2 = 1 - v_3$ at equilibrium are 0.7059, 0.1191, and 0.0459. At $x_2 = 15$ they are 0.4925, 2.400×10^{-3}, and 0.883×10^{-3}. For $x_2 \geq 20$ and $x_3 \geq x_2$ the volume fractions v_2 are negligible.

Although, according to the calculations cited, the rejection of component 2 from the isotropic phase is pronounced even at moderate concentrations of solutes for large x_2 (see the isotropic binodial in Figure 4 at $1 - v_1 = 0.2$, for example), it is not as severe as the rejection of the random coil from the anisotropic phase. This is evident from the phase diagrams for the ternary systems shown in Figures 1–4. It is demonstrated further by the declining dashed curve in Figure 6 showing v_3'/v_2, or $v_3'/(1 - v_3)$, plotted on the logarithmic scale along the right-hand ordinate as a function of x_2 for the binary systems 2,3 in which $x_3 = x_2$. Thus, as $x_2 = x_3$ increases, v_2 in the isotropic phase of the binary system, though very small, becomes manifoldly greater than v_3' in the conjugate nematic phase.

The severity of the preferential partitioning of the respective solutes between the two phases in the ternary systems is shown further by the inclinations of the tie lines in Figures 1–4 to the straight lines (not shown) extending from apex 1 through the tie line termini on the binodial for the isotropic phase. Thus, the ratio v_3/v_2 for the isotropic phase is much greater than v_3'/v_2' for its nematic conjugate phase. Although this feature is more pronounced the larger the value of x_2, it is conspicuous even at $x_2 = 10$. As noted above, it is accentuated by an increase in x_3.

Discussion

The marked discrimination between the disparate solute species by the coexisting isotropic and anisotropic phases clearly is the most striking result demonstrated by the calculations presented above. The two solute species considered represent extremes, the one being rigid and rodlike and the other sufficiently flexible to adopt a random-coiled configuration.[4] The underlying basis for the differentiation between them is manifest in the primary derivations of the configuration partition function.[1,3] The diverse behaviors can be traced through the terms in y appearing in the chemical potentials for the anisotropic phase (see eq 9–11) and comparison with their counterparts for the isotropic phase (see eq 12–14). From a physical point of view, the isotropic phase offers to a rodlike solute none of the advantages of orientation. Hence, this component prefers the anisotropic phase where obstruction by neighboring species is alleviated by mutual alignment. To an even greater degree, intrusion of the random coil into the anisotropic phase tends to impose overlaps that are not mitigated by the prevailing orientation.

The anisotropic phase approaches the selectivity of a pure crystal in its rejection of a foreign component, in this case the random coil. For a large axis ratio (e.g., for $x_2 = x_3 = 100$) a high degree of selectivity occurs even at relatively low concentrations, where the volume fraction of solvent exceeds that of the rodlike solute severalfold.

The results of this investigation have obvious implications with reference to helix–coil transitions at concentrations conducive to separation of a nematic phase.

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Statistical Thermodynamics of Mixtures of Rodlike Particles. 6. Rods Connected by Flexible Joints

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ABSTRACT: Solutions are treated in which the solute molecule comprises m rodlike sequences, each of axis ratio x, connected in linear succession by $m - 1$ joints permitting free orientations. Separation of an anisotropic phase depends predominantly on x. Increasing the chain length from x to $x_m = mx$ by joining m rods affects the compositions of the phases coexisting at equilibrium by only a few percent. The implications of these results on the behavior to be expected in systems of semirigid real chains of various types are discussed.

Chain molecules, however constituted, invariably possess some degree of flexibility. Even in instances, exemplified by poly(p-phenylene), where the skeletal bonds are nominally collinear, bending of bond angles must introduce a finite degree of flexibility. Stable helical conformations, such as those of the polypeptide α helix and of double-stranded DNA, likewise are subject to small, random departures of their helical axes from strict rectilinearity. The cumulative effect of these deviations throughout a very long chain may be substantial. In particular, the

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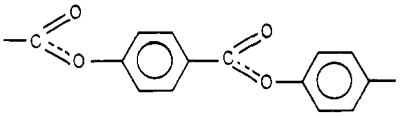
otherwise rigid, rectilinear chain requires characterization by a finite persistence length.

Examples of highly extended structures in which small differences in valence angles in conjunction with alternative rotations about skeletal bonds conspire to conduce departures from rectilinearity are furnished by poly(*p*-hydroxybenzoic acid)



and the corresponding polyamide, poly(*p*-aminobenzoic acid). The ester groups (and the amide groups as well) occur overwhelmingly in the trans-planar configuration. Bond angles at the carbonyl (C=O) and at the skeletal oxygen atom differ by about 3°. Although such chains are highly extended in the direction of the *p*-phenylene axis, rotations about these axes introduce randomness in the *propagation of the chain in transverse directions*. The small differences in skeletal bond angles, augmented by bond angle bending, introduce further departures from representation as a rigid rod.

The studies presented in this paper were carried out for the purpose of examining, in a first approximation, the effects of departures from strict rigidity briefly illustrated by the examples cited. The model chosen is a familiar one. It consists of a series of rigid rods connected by freely flexible joints. Directions of successive rods thus joined are unconstrained by the model. Such correlations between rods as may occur in a system of many such molecules are imposed through intermolecular encounters; intramolecular constraints on orientations are absent.

Justification for this simple model as a representation of any real chain rests on the supposition that the cumulative effect of many small departures from rectilinearity over a length of the real chain equal to a rodlike member of the model can be represented by the junction between two such members, that junction having the quality of permitting free orientation. The model will be recognized as the one introduced originally by Kuhn[1] and subsequently widely used in attempts to treat the configurational characteristics of polymer chains having the usual degree of flexibility. It appears to be better suited to the restricted class of semirigid chains under consideration here than to the more common ones to which it has frequently been applied.

We take all rods to be of the same length. They are characterized by an axis ratio x. The model comprising m such rods connected as described is deemed appropriate for chains of uniform structure in which deviations from rectilinearity, averaged over time, are the same throughout their lengths. The present treatment could be elaborated by the methods presented in preceding papers of this series to deal with linearly connected rods that are distributed in length x. As is pointed out in the Discussion, the results of extension of the theory in this direction can be anticipated from the results presented here.

Theory

The expected number of locations for the jth molecule added to the lattice consisting of n_0 sites is, according to the methods[2] employed in papers 1[3] and 5[4] of this series,

$$\nu_j = \left\{\frac{[n_0 - mx(j-1)]!}{(n_0 - mxj)!}\right\}\left[\frac{1}{n_0^{my-1}}\right]\left\{\frac{[n_0 - m(x-y)j]!}{[n_0 - m(x-y)(j-1)]!}\right\} \tag{1}$$

where x is the axis ratio of each of the m rods comprising the molecule as represented by the model defined above. The first quantity in braces takes account of the total number of vacant sites required for the accommodation of molecule j.[3] The first of these factors, namely, $n_0 - mx(j - 1)$, expresses the total number of vacant sites, each of which is eligible for the first segment of this molecule. Division of each of $my - 1$ of the remaining factors by n_0 furnishes the required product of volume fraction expectations of vacancies in the sites selected for every initial segment of the submolecules[3] of the chain beyond the first. Combination of the remaining $m(x - y)$ factors from the first expression in braces with the equal number of factors given by the ratio of factorials in the last quantity in braces in eq 1 gives the product of number fraction expectations of vacancies in all sites required for segments beyond the first in each of the my submolecules of the chain.[3]

Adapting eq 1-4 to a system consisting of the species here considered, we write

$$Z_{\mathrm{M}} = [\prod_1^{n_2}\nu_j/n_2!][(mn_2)!\prod_k \omega_k^{\xi_k}/\xi_k!] \tag{2}$$

where n_2 is the total number of solute molecules and ξ_k is the number of their mn_2 rodlike members oriented within a range of solid angle of measure ω_k relative to the solid angle within which $y = 1$. Replacing the second factor in brackets by y^{2mn_2}, in keeping with the corresponding approximation used in the preceding papers,[2,3] we obtain

$$Z_{\mathrm{M}} = \frac{(n_1 + ymn_2)!y^{2mn_2}}{n_1!n_2!(n_1 + x_m n_2)^{n_2(my-1)}} \tag{3}$$

where $x_m = mx$ is the total number of segments in the solute molecule. Introduction of Stirling's approximation yields

$$-\ln Z_{\mathrm{M}} = n_1 \ln v_1 + n_2 \ln (v_2/x_m) - (n_1 + x_m n_2)[1 - v_2(1 - y/x)] \ln [1 - v_2(1 - y/x)] - n_2(m \ln y^2 - my + 1) \tag{4}$$

Equating $\partial \ln Z_{\mathrm{M}}/\partial y$ to zero, we again obtain[2,3]

$$\exp(-2/y) = 1 - v_2(1 - y/x) \tag{5}$$

The expressions for the chemical potentials that follow from eq 4 are, after substitution from eq 5,

$$(\mu_1 - \mu_1{}^0)/RT = \ln (1 - v_2) + 2/y + v_2(y/x - 1/x_m) \tag{6}$$

and

$$(\mu_2 - \mu_2{}^0)/RT = \ln (v_2/x_m) + v_2 x_m(y/x - 1/x_m) + 2m(1 - \ln y) \tag{7}$$

It will be understood that y in eq 6 and 7 is to be identified with its equilibrium value given by eq 5. If $m = 1$, eq 6 reduces to eq 1-22 appropriately modified for a monodisperse system, i.e., with $v_{2\mathrm{R}} = 0$, $v_{2\mathrm{A}} = v_2$, and $\bar{x}_{n\mathrm{A}}$ replaced by $x_m = x$. Similarly, eq 7 reduces to eq 1-24 in this case, with v_x replaced by v_2 in the latter equation. It will be apparent that eq 6 for the chemical potential of the solvent differs from that for the corresponding mixture of disconnected rods of axis ratio x only through replacement of the term v_2/x by v_2/x_m. This term underlies the first term in the virial expansion of the osmotic pressure. Its counterparts likewise distinguish the expression for μ_2 from that for independent rods obtained by setting $m = 1$ and $x_m = x$.

The chemical potentials for an isotropic phase deduced from eq 4 with $y = x$ are

$$(\mu_1 - \mu_1{}^0)/RT = \ln (1 - v_2) + v_2(1 - 1/x_m) \tag{8}$$

$$(\mu_2 - \mu_2{}^0)/RT = \ln (v_2/x_m) + v_2(x_m - 1) - 2m \ln x \tag{9}$$

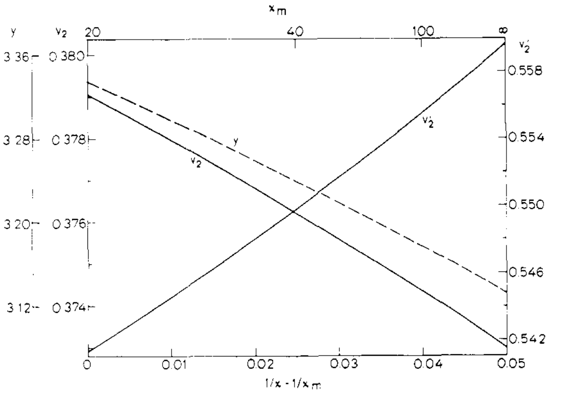


Figure 1. Values of v_2, v_2', and y (dashed line) plotted against the function $1/x - 1/x_m$ of the total length $x_m = mx$ of the chain consisting of m rods of axis ratio $x = 20$, with x_m increasing from 20 to ∞.

These may be compared with the renditions of eq 1-27 and 1-28 as modified for a monodisperse solute.

The equations for phase equilibrium are

$$\ln\left(\frac{1-v_2'}{1-v_2}\right) = v_2(1 - 1/x_m) - v_2'(y/x - 1/x_m) - 2/y \tag{10}$$

(compare with eq 1-30 and eq 5-15 with $v_3 = 0$), and

$$\ln(v_2'/v_2) = x_m[v_2(1 - 1/x_m) - v_2'(y/x - 1/x_m)] - 2m[1 + \ln(x/y)] \tag{11}$$

(compare with eq 1-33 and eq 5-16 with $v_3 = 0$). Combination of eq 10 and 11 gives

$$\ln\left(\frac{1-v_2'}{1-v_2}\right) = \left(\frac{1}{x_m}\right)\ln\left(\frac{v_2'}{v_2}\right) - \frac{2}{y} + \left(\frac{2}{x}\right)[1 + \ln(x/y)] \tag{12}$$

Equations 10–12 revert to the corresponding expressions for simple rods upon replacing x_m by x. The terms affected are small for $x >> 1$.

Calculations

Equations 5, 10, and 11 provide the basis for numerical calculations of phases in equilibrium, with eq 12 a preferred alternative to eq 11. In Figure 1 volume fractions v_2 and v_2' of solute in the coexisting isotropic and anisotropic phases, respectively, are plotted as a function of x_m for fixed $x = 20$. The function chosen for the abscissa, namely, $1/x - 1/x_m = (m - 1)/x_m$, is a measure of the difference between the number of rodlike members and the number of independent molecules. Values of y are shown by the dashed line.

As the chain is lengthened by increasing the number of rods it contains from $m = 1$ ($x_m = x = 20$) to $m = \infty$ ($x_m = \infty$) the volume fraction v_2 of solute in the isotropic phase decreases and v_2' for the anisotropic phase increases. Hence, the immiscibility gap is broadened as the chain is lengthened in the stated manner. As Figure 1 shows, however, these changes are small. The phase equilibrium depends principally on the axis ratio x of the rodlike member. It is affected only to a minor degree by joining rods, of given x, one to another with flexible joints.

Calculations at other values of x lead to the same conclusions. These further calculations are summarized in Figure 2. The upper curve records the decrease in v_2 when x_m is increased from x to ∞, this decrease being expressed relative to the value of v_2 for $m = 1$, i.e., for $x_m = x$. The lower curve similarly represents the increase in v_2' for the same change in x_m, the increase being expressed relative to v_2' for $x_m = x$. These changes increase with x commencing at $x = 6.70183$, the axis ratio for incipience of phase separation (occurring at $v_2 = v_2' = 1$). For large x_m they approach asymptotes in the vicinity of −3% for Δv_2 and of 10% for v_2'.

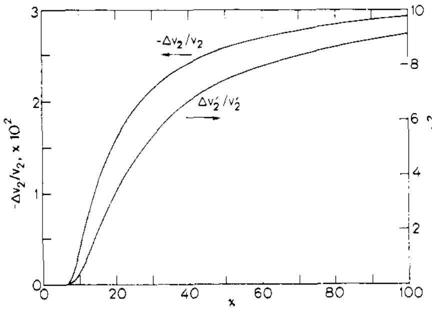


Figure 2. Relative changes in v_2 and in v_2' when x_m is increased from x to ∞, corresponding to an increase of m from 1 to ∞, plotted against x. The ordinates are $-\Delta v_2/v_2$ and $\Delta v_2'/v_2'$, respectively, where v_2 and v_2' refer to $x_m = x$ (i.e., $m = 1$).

Discussion

It is a well-established principle of polymer solution theory that the effect of finite chain length on thermodynamic properties, relative to other influences, diminishes as the concentration is increased. The effect becomes negligible at concentrations such that each molecule of the solute is, on the average, engaged in interactions with many other solute molecules. Only at concentrations sufficiently low to reduce such "overlaps" to low incidence does the finite chain length (hence, the finite number of discrete molecules) assume dominance. The concentration regime for transition from one pattern of behavior to the other depends on the chain length.

Separation of a nematic phase requires a concentration well above this transitional range. At the incident concentrations the dependence of the chemical potentials on overall chain length is superseded by interactions of higher order, i.e., the chemical potentials depend on higher powers of the concentration. In the familiar language of the virial expansion of the chemical potential, it is the higher virial coefficients that are dominant; the first coefficient, which embodies the dependence on chain length, has receded to a role of secondary importance. In fact, the virial expansion converges slowly at the concentrations required for phase separation, and hence is an unattractive device for quantitative treatment of the phase separation.

The small influence of the overall chain length $x_m = mx$ on the phase separation is readily comprehensible on this basis. The length of the rigid segment is clearly implicated as the overriding determinant.

Application of this deduction from the analysis of an artificial model to real chain molecules should be undertaken with caution. Examples conforming precisely to the model probably do not exist. Nevertheless, as mentioned in the introduction, some classes of rigid chains probably can be satisfactorily approximated by it through judicious choice of the rodlike segment and its axis ratio x. Specifically, the persistence length of a chain that tends to propagate along a rectilinear axis but which departs therefrom through the frequent occurrence of small, random deviations, successive deviations being uncorrelated, may be presumed to afford a measure of the length of the effective segment and its axis ratio x.[5]

The role of small, random deviations from the preferred conformation as the principal agency of departure from rectilinearity presupposes a homopolymeric chain of uniformly repeating structure. Hence, it is legitimate to adopt an equivalent rodlike segment of the same length and axis ratio x for all chains as well as for all portions of a given chain. It follows that the immiscibility gap should be small, as asserted by the treatment above, regardless of the polydispersity of the overall molecular chain lengths. Only if this distribution includes an appreciable fraction of species of length less than x for the rodlike segment should the immiscibility gap be subject to the marked effects of polydispersity found in parts 2[6] and 3[7] for large differences in axis ratios of rigid rodlike components.

Chains whose trajectories cannot be characterized simply by a scalar magnitude expressing the persistence in the preferred direction, but must instead be characterized by a persistence vector[8] embedded in the unit of reference, elude quantitative representation by any simple model of the sort adopted here. The correlations of curvature transmitted along such chains (exemplified by syndiotactic poly(methyl methacrylate)) require a more elaborate scheme.[9,10] However, chains of this type may seldom possess both the regularity of form and the rigidity that are required for the formation of a mesophase.

Departures from rigid rectilinearity may occur, alternatively, through occasional incidence of sharp bends in an otherwise rodlike chain. A polypeptide chain that is predomantly α helical, but which contains a few units that are not incorporated in α-helical sequences, is illustrative of this case. Since these bends are well separated along the chain, they will ordinarily occur more or less at random. Hence, the distribution of uninterrupted rigid sequences should conform, approximately, to the most probable distribution treated in 3.[7] Inferring from the results of the present paper that joining such rigid sequences into long chains should have only a minor effect on the phase equilibrium, we may anticipate a very large immiscibility gap in such instances owing to the great variability in lengths x of the rodlike segments required for representation of the chain by the freely jointed model.

It should not be concluded, however, that the results of paper 3[7] are precisely applicable to chains of the type identified in the paragraph above. The directions of successive rigid sequences in such chains will be subject, in general, to substantial correlations, e.g., the angle between successive rodlike sequences will be dictated by the structure and conformation at the bend. The connections between rigid sequences cannot, therefore, be represented by free joints. The results of the present paper are strictly valid only for rigid segments thus connected. The principal conclusion that connection of rods one to another in linear succession has only a minor effect on the phase equilibria should not be assumed to hold for connections that impose constraints on the direction assumed by a rigid sequence relative to its predecessor in the chain.

The foregoing difficulty appears not to be amenable to resolution by any device applicable generally to all types of chains in the broad category of those in which the directions of successive rigid sequences are somehow correlated. A model for a limited class of "semiflexible" chains of this kind was presented previously.[11]

Block copolymers in which one of the blocks is a rigid chain represent a further class of substances having the potentiality for formation of a nematic phase. Here the presence of a succession of flexible units separating successive rigid sequences assures independence of the directions of the latter. Hence, the axis ratios of the rigid sequences, together with their combined volume fraction, should be the principal determinants of the thermodynamic properties, including the propensity for phase separation. The distribution of these axis ratios must be considered; see 3[7] and 4.[12] If, as may frequently occur, the sequences of the rigid component are represented by a most probable distribution, then appearance of a nematic phase may require a relatively low mean axis ratio $\bar{x}_n$, owing to the polydispersity in the lengths of these sequences (see 3[7]). The nonrigid blocks between rigid sequences may be expected to act, collectively, as a random-coil component. We infer from the results of the preceding paper (5),[4] therefore, that dilution of the rodlike component with the nonrigid chains comprising the "soft" blocks should have a relatively small effect on the tendency to form a nematic phase. In other words, the effect of dilution by the soft component may be largely compensated by the hostility of the amorphous (i.e., isotropic) phase to rigid sequences.[4]

This latter case is one that invites further investigation by extension of the methods applied in this series of papers.

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