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References and Notes

(1) P. J. Flory and A. Abe, *Macromolecules*, companion paper in this issue, part 1.

(2) P. J. Flory, *Proc. R. Soc. London, Ser. A.*, **234**, 73 (1956).

(3) It follows from eq 1-35, -38–40, and -32 that $\ln \Gamma \approx \eta\,(x_a - x_b)$ for $(x_a - x_b) \gg 1$. Moreover, as eq 1-41 indicates, $\eta \approx v_2$. Numerical calculations confirm this approximation, except at volume fractions v_2 approaching the upper limit for $\gamma = 1$, where the approximation fails altogether. Hence log Γ should be very nearly linear in v_2 over most of the range, as the computations shown in Figures 2, 5, and 7 confirm for the systems investigated.

Statistical Thermodynamics of Mixtures of Rodlike Particles. 3. The Most Probable Distribution

Paul J. Flory* and Randall S. Frost

Department of Chemistry, Stanford University, Stanford, California 94305.

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ABSTRACT: Biphasic equilibria are investigated for athermal mixtures in which the solute comprises rodlike particles having the familiar distribution $v_x^0 = v_2^0(1-p)^2 x p^{x-1}$, x being both the number of units and the axis ratio. Under conditions such that the volumes of the coexisting phases are comparable, the polydispersity in each phase is considerably lower than for the parent ("most probable") distribution. Fractionation between the phases is remarkably efficient. A concomitant of the preferential partitioning of lower and higher species between the respective phases is the broad range of overall concentration within which the system is biphasic. The undiluted polydisperse solute is predicted to be biphasic for $(1-p)^{-1}$ in the range ~2.3–17.5. It is isotropic below this range and wholly anisotropic for greater average chain lengths $\bar{x}_n^0$. According to theory, an isotropic phase in which the solute retains the foregoing distribution can coexist in equilibrium with an anisotropic (nematic) phase only if this phase comprises species of very large x at high concentration in ordered array. This deduction follows regardless of the average $\bar{x}_n^0 = (1-p)^{-1}$ in the isotropic phase provided only that $\bar{x}_n^0 > 2.3$. If interchange processes $M_{x_1} + M_{x_2} \rightleftarrows M_{x_1+x_2}$ occur freely at random, continuous transformation to a highly ordered anisotropic phase is predicted. Thus, formation of rodlike particles through random, linear aggregation of subunits offers an exceptionally simple scheme for self-ordering.

In this paper we treat the partitioning of a so-called "most probable" distribution of rodlike particles between isotropic and anisotropic phases. As in the preceding papers, 1[1] and 2,[2] exchange interactions between solute particles are assumed to be null. Hence, only the spaciogeometric requirements of the solute particles are considered.

The most probable distribution for particles consisting of x units is specified by

$$v_x^0/v_2^0 = (1-p)^2 x p^{x-1} \qquad (1)$$

where p may be considered to be the expectation of perpetuation of a sequence of units to include at least one more unit, $1-p$ being the expectation of termination of the sequence. The zero superscripts signify the unpartitioned distribution; v_2^0 denotes the mean volume fraction of solute in both phases combined, and v_x^0 the corresponding volume fraction of species x in the system as a whole. The number average size, or axis ratio, is

$$\bar{x}_n^0 \equiv \sum v_x^0 / \sum x^{-1} v_x^0 = (1-p)^{-1} \qquad (2)$$

Theoretical Relationship for Phase Equilibria

1. Equations of Conservation. Let V and V' denote the volumes of the isotropic and anisotropic phases, respectively; v_2 and v_2' will denote the respective volume fractions of solute in these phases. Then

$$\Phi v_2 + (1-\Phi)v_2' = v_2^0 \qquad (3)$$

where Φ is the ratio of the volume of the isotropic phase to the total volume, i.e.,

$$\Phi = V/(V+V') = V/V^0 \qquad (4)$$

Similarly,

$$\Phi v_x + (1-\Phi)v_x' = v_x^0 \qquad (5)$$

Hence, for the distribution considered (see eq 1)

$$\Phi v_x + (1-\Phi)v_x' = v_2^0(1-p)^2 x p^{x-1} \qquad (5')$$

Also

$$\Phi v_2/\bar{x}_n + (1-\Phi)v_2'/\bar{x}_n' = v_2^0/\bar{x}_n^0 = v_2^0(1-p) \qquad (6)$$

2. Systems at Equilibrium Disorder ($y = y_{\text{eq}}$). In this most general case we take $y = y_{\text{eq}}$, disregarding the possibility that y_{eq} may be less than unity.[1,2]

Consider first the solute species with $x \le y$, where $y = y_{\text{eq}} > 1$. Substitution from eq 1–35 for v_x in eq 5′ gives

$$v_x'/v_2^0 = \Phi^{-1}(1-p)^2 x p^{x-1}/[e^{\zeta x} + (1-\Phi)\Phi^{-1}], \quad x \le y \qquad (7)$$

ζ being defined by eq 1–36. Hence,

$$v_{2\text{R}}'/v_2^0 = \Phi^{-1}(1-p)^2 I_{1\text{R}} \qquad (8)$$

where

$$I_{1\text{R}} = \sum_{1}^{x \le y} x p^{(x-1)}/[e^{\zeta x} + (1-\Phi)\Phi^{-1}] \qquad (9)$$

The number average of x for species in this category is

$$\bar{x}_{n\text{R}}' = I_{1\text{R}}/I_{0\text{R}} \qquad (10)$$

where

$$I_{0\text{R}} = \sum_{1}^{x \le y} p^{x-1}/[e^{\zeta x} + (1-\Phi)\Phi^{-1}] \qquad (11)$$

Similarly for species with x exceeding y we have from eq 5′ and 1–38

$$v_x'/v_2^0 = \Phi^{-1}(y/e)^2(1-p)^2 x p^{x-1}/ [x^2 e^{-\eta x} + (y/e)^2(1-\Phi)\Phi^{-1}], \quad x > y \qquad (12)$$

η being defined by eq 1–39 or 1–40. Then

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$$v_{2A}'/v_2^0 = \Phi^{-1}(y/e)^2(1-p)^2 I_{1A} \tag{13}$$

where

$$I_{1A} = \sum_{x>y} xp^{x-1}/[x^2e^{-\eta x} + (y/e)^2(1-\Phi)\Phi^{-1}] \tag{14}$$

and

$$\bar{x}_{nA}' = I_{1A}/I_{0A} \tag{15}$$

where

$$I_{0A} = \sum_{x>y} p^{x-1}/[x^2e^{-\eta x} + (y/e)^2(1-\Phi)\Phi^{-1}] \tag{16}$$

Combination of results for the two categories of species gives

$$v_2'/v_2^0 = v_{2R}'/v_2^0 + v_{2A}'/v_2^0 \tag{17}$$

and

$$v_2'/\bar{x}_n' = v_{2R}'/\bar{x}_{nR}' + v_{2A}'/\bar{x}_{nA}' \tag{18}$$

or

$$1/\bar{x}_n' = (v_2'/v_2^0)^{-1}[(v_{2R}'/v_2^0\bar{x}_{nR}') + (v_{2A}'/v_2^0\bar{x}_{nA}')] \tag{18'}$$

Additionally, we have from 1-12′, the equation that specifies the equilibrium value of y,

$$v_{2A}' = [1 - \exp(-2/y)]/(1 - y/\bar{x}_{nA}') \tag{19}$$

From eq 1-32 and 1-36, which latter follows directly from the equilibrium condition $\mu_1 = \mu_1'$ (see eq 1-30),

$$\zeta = 2/y - v_2(1 - 1/\bar{x}_n) + v_{2R}'(1 - 1/\bar{x}_{nR}') + v_{2A}'(y-1)/\bar{x}_{nA}' \tag{20}$$

or (see eq 1-39),

$$\eta = v_2(1 - 1/\bar{x}_n) - v_{2R}'(1 - 1/\bar{x}_{nR}') - v_{2A}'(y-1)/\bar{x}_{nA}' \tag{20'}$$

Finally, rearrangement of eq 1-36 and multiplication by v_2^0 gives

$$v_2^0 = [\exp(\zeta) - 1]/[(v_2'/v_2^0)\exp(\zeta) - v_2/v_2^0] \tag{21}$$

Let p and Φ be given. Equation 2 fixes $\bar{x}_n^0$. All other quantities characterizing the phases in equilibrium are then determined by the relations given in this section. These quantities may be evaluated numerically according to the following procedure:

(i) Choose trial values of y and ζ.

(ii) Evaluate the summations giving I_{0R}, I_{1R}, I_{0A}, and I_{1A} according to eq 11, 9, 16, and 14, respectively. Calculate v_{2R}'/v_2^0, v_{2A}'/v_2^0, $\bar{x}_{nR}'$, and $\bar{x}_{nA}'$ using eq 8, 13, 10, and 15, respectively. From eq 17 obtain v_2'/v_2^0; eq 3 then gives v_2/v_2^0.

(iii) Evaluate v_2^0 from eq 21. Values of v_{2R}', v_{2A}', v_2, and v_2' are then obtained from the ratios above.

(iv) From $\bar{x}_{nA}'$ and the trial value of y calculate v_{2A}' according to eq 19. Compare with the value above.

(v) Choose another value of ζ and repeat steps (ii)-(iv), etc., until agreement is achieved at step (iv) within an admissible limit.

(vi) Calculate $1/\bar{x}_n'$ from eq 18′ and substitute the result in eq 6 to obtain $1/\bar{x}_n$.

(vii) Use eq 20 to calculate y from the results obtained above. Compare y thus calculated with the trial y.

(viii) Choose another trial value of y and repeat steps (ii)-(vii), etc., until agreement is achieved at step (vii) within an acceptable tolerance.

3. Systems in which the Anisotropic Phase is Ideal ($y = 1$). If eq 1-12 or 1-12′ yields a value $y < 1$, then, for reasons given in 1, it may be appropriate to set $y = 1$, thereby rendering the anisotropic phase ideal. Equations 1-43 and 1-44 furnish the basis for treating phase equilibria in this case.

Substitution of eq 1-44 in 5′ gives

$$\frac{v_x'}{v_2^0} = \frac{D(1-\Phi)^{-1}(1-p)^2xp^{x-1}}{x^2\exp(-\eta^*x) + D} \tag{22}$$

where

$$D = (1-\Phi)\Phi^{-1}[1 - v_2'(1 - 1/\bar{x}_n')] \tag{23}$$

and (see eq 1-45)

$$\eta^* = (1 - 1/\bar{x}_n)v_2 \tag{24}$$

Then

$$v_2'/v_2^0 = D(1-\Phi)^{-1}(1-p)^2I_1 \tag{25}$$

and

$$\bar{x}_n' = I_1/I_0 \tag{26}$$

where

$$I_0 = \sum_1^\infty p^{x-1}/[x^2\exp(-\eta^*x) + D] \tag{27}$$

$$I_1 = \sum_1^\infty xp^{x-1}/[x^2\exp(-\eta^*x) + D] \tag{28}$$

Solution of eq 23 for v_2' gives

$$v_2' = [1 - (1-\Phi)^{-1}\Phi D](1 - 1/\bar{x}_n')^{-1} \tag{23'}$$

Substitution of eq 23′ in 25 yields

$$v_2^0 = (1 - \Phi - \Phi D)/DI_1(1-p)^2(1 - 1/\bar{x}_n') \tag{29}$$

Substitution of eq 23′ and 29 in eq 3 leads to

$$v_2 = [(1-\Phi)\Phi^{-1} - D][1/DI_1(1-p)^2 - 1](1 - 1/\bar{x}_n')^{-1} \tag{30}$$

According to eq 1-43 and the definition of η' given by eq 24,

$$\exp(\eta') = (1 - v_2')/(1 - v_2)[1 - v_2'(1 - 1/\bar{x}_n')] \tag{31}$$

Substitution from eq 23′ and 30 for v_2' and v_2, respectively, and solution of the resulting equation for Φ yields, after substitution for $\bar{x}_n'$ from eq 26,

$$\Phi^{-1} = 1 + D + D(I_1 - I_0)(1 - e^{-\eta^*})/[(1-p)^{-2} - I_0e^{-\eta^*} - DI_1] \tag{32}$$

By solving eq 6 for $1/\bar{x}_n$ and substituting from eq 23′ for v_2', from eq 29 for v_2^0, from eq 30 for v_2, and from eq 26 for $\bar{x}_n'$ one obtains

$$1/\bar{x}_n = (1-p) + D[I_1(1-p) - I_0]/[(1-p)^{-2} - DI_1] \tag{33}$$

Solution of the preceding equations for specified values of p and D may be carried out as follows:

(i) Choose a trial value of η^*.

(ii) Calculate I_0 and I_1 according to eq 27 and 28. Obtain $\bar{x}_n'$ from eq 26.

(iii) Calculate Φ and $\bar{x}_n$ according to eq 32 and 33; obtain v_2 from eq 30.

(iv) Calculate η^* according to eq 24 from $\bar{x}_n$ and v_2. Compare η^* thus obtained with the trial η^*.

(v) Repeat steps (i)-(iv) with another trial η^*, etc., until agreement is obtained within prescribed limits.

(vi) Calculate v_2' and v_2^0 from eq 23′ and 29, respectively.

4. The Limiting Case $\Phi = 1$. In this limit

$$v_2 = v_2^0 \tag{34}$$

and the solute in the isotropic phase retains the most probable distribution; i.e.,

$$\bar{x}_n = \bar{x}_n{}^0 = (1 - p)^{-1} \tag{35}$$

We seek the composition of the coexisting anisotropic phase, the quantity of which is infinitesimal if it is formed subject to the stated condition. The extent of this phase could, of course, be increased at fixed composition without vitiating equilibrium with the isotropic phase whose composition is specified by v_2 and p. Hence, the composition to be determined may be expected to represent that of the anisotropic phase coexisting with an isotropic phase in which the solute has the most probable distribution, irrespective of the quantities of the two phases.

Consider the case $y = y_{\text{eq}}$. We anticipate that y will be small and hence that the randomly oriented species denoted by R may be ignored. Then the sums $I_{0\text{R}}$ and $I_{1\text{R}}$ may be dismissed and those given by eq 16 and 14 reduce in the limit $\Phi \rightarrow 1$ to

$$I_0 = p^{-1}\sum_1^\infty x^{-2}s^x \tag{36}$$

$$I_1 = p^{-1}\sum_1^\infty x^{-1}s^x \tag{37}$$

where

$$s = p \exp(\eta) \tag{38}$$

Values of $s > 1$ fall in the domain of equilibria for $0 \leq \Phi < 1$. Substitution of $s > 1$ in eq 36 gives infinite I_0, which is clearly inadmissible, for it would imply divergence in the number distribution. It may be shown that solutions of the equations for phase equilibria do not exist for $s < 1$. We therefore examine $s = 1$ as the solution when $\Phi = 1$.

Approaching the limit from $s < 1$, one obtains

$$I_0 = \pi^2/6p$$

$$I_1 = -p^{-1} \ln (1 - s) = \infty$$

at the limit $s \rightarrow 1$. Hence,

$$1/\bar{x}_n{}' = 0 \tag{39}$$

in the limit $\Phi \rightarrow 1$. It follows from eq 20′ and 35 that

$$\eta = pv_2$$

in this limit. Hence, from eq 38

$$v_2 = -p^{-1} \ln p \tag{40}$$

According to eq 13

$$\lim_{\Phi\rightarrow 1} (y^2 I_1) = e^2(1 - p)^{-2}(v_2{}'/v_2{}^0) \tag{41}$$

Obviously, $(v_2{}'/v_2{}^0) > 0$ at $\Phi = 1$. Moreover, $v_2{}^0 \neq 0$ since $v_2{}^0 = v_2 = \eta p^{-1} = 0$ would require $\eta = 0$ and, hence, $s = p < 1$. We conclude, therefore, that $(y^2 I_1)$ is finite in the limit $\Phi \rightarrow 1$. It follows that

$$y = 0 \tag{42}$$

and, from eq 19,

$$v_2{}' = 1 \tag{43}$$

in this limit.

Equation 40 specifies the unique concentration of the isotropic phase containing rodlike solute species having the most probable distribution, characterized by p, that is required for equilibrium with an anisotropic phase. The character of the coexisting anisotropic phase is specified by eq 39, 42, and 43. In particular, eq 40 may be presumed to express the threshold concentration for incipient separation of an anisotropic phase from an isotropic solution of rodlike particles of the specified distribution. Numerical calculations presented below reveal the need for qualification of this relationship as applied to a real system of finite size, however.

Similar results are obtained for the system at equilibrium with an anisotropic phase which is ideal ($y = 1$). In the limit $\Phi \rightarrow 1$, $D \rightarrow 0$ according to eq 23. Hence, eq 27 and 28 for I_0 and I_1 reduce to eq 36 and 37 with s defined by eq 38, η therein being replaced by η^*. By arguments analogous to those above, $s = 1$ and $\bar{x}_n{}' = \infty$ in the stated limit. According to eq 24 and 35, $\eta^* = pv_2$. Equation 40 applies identically therefore to this system. According to eq 25, the quantity $DI_1(1 - \Phi)^{-1}$ reaches a finite limit as $\Phi \rightarrow 1$. Hence, $D(1 - \Phi)^{-1} = 0$ in this limit. It follows from eq 23′ that $v_2{}' \rightarrow 1$. Hence, eq 39, 40, and 43 hold also for this system.

5. The Limiting Case $\Phi = 0$. In this limit $v_2{}' = v_2{}^0$ and

$$\bar{x}_n{}' = \bar{x}_n{}^0 = (1 - p)^{-1} \tag{44}$$

The equations in sections 2 and 3 are inapplicable when $\Phi = 0$. Hence, the required relationships must be recast as follows.

We consider first systems in which $y = y_{\text{eq}}$. Then from eq 1 and 1–35 we obtain

$$v_x = v_2{}'(1 - p)^2 p^{-1} x b^x, \quad x \leq y \tag{45}$$

where $b = p \exp(\zeta)$, and from eq 1 and 1–38

$$v_x = v_2{}'(1 - p)^2 p^{-1}(e/y)^2 x^3 a^x, \quad x > y \tag{46}$$

where $a = p \exp(-\eta)$. Let

$$J_0 \equiv p^{-1}[\sum_{x=1}^{y^*} b^x + (e/y)^2 \sum_{x>y^*} x^2 a^x] = \\ p^{-1}\{(e/y)^2 \sum_1^\infty x^2 a^x + \sum_{x=1}^{y^*} [b^x - (e/y)^2 x^2 a^x]\} = \\ p^{-1}\{(e/y)^2 a(1 + a)(1 - a)^{-3} + \sum_{x=1}^{y^*} [b^x - (e/y)^2 x^2 a^x]\} \tag{47}$$

where y^* is the largest integer $\leq y$. Similarly let

$$J_1 \equiv p^{-1}[\sum_{x=1}^{y^*} x b^x + (e/y)^2 \sum_{x>y^*} x^3 a^x] = p^{-1}\{(e/y)^2 \times \\ (a + 4a^2 + a^3)(1 - a)^{-4} + \sum_{x=1}^{y^*} [x b^x - (e/y)^2 x^3 a^x]\} \tag{48}$$

Then

$$v_2 = v_2{}'(1 - p)^2 J_1 \tag{49}$$

$$\bar{x}_n = J_1/J_0 \tag{50}$$

Also,

$$v_{2\text{A}}{}' = v_2{}'(1 - p)^2 \sum_{x>y^*} x p^{x-1} = v_2{}' p^{y^*}[y^*(1 - p) + 1] \tag{51}$$

$$\bar{x}_{n\text{A}}{}' = v_{2\text{A}}{}'/v_2{}'(1 - p)^2 \sum_{x>y^*} p^{x-1} = (1 - p)^{-1} + y^* \tag{52}$$

and of course $v_{2\text{R}}{}'$ and $\bar{x}_{n\text{R}}{}'$ can be obtained from $v_2{}'$, $v_{2\text{A}}{}'$, $\bar{x}_n{}' = (1 - p)^{-1}$, and $\bar{x}_{n\text{A}}{}'$. Equations 19 and 20′ are directly applicable. Equations 1–36 and 1–39 give

$$\ln [(1 - v_2{}')/(1 - v_2)] = \eta - 2/y \tag{53}$$

These equations may be solved by a procedure similar to that described in section 2. Given p and $\Phi = 0$, trial values of y and η are chosen. The latter quantity, in conjunction with p and y, determines a, b, and ζ. Hence, J_0 and J_1 may be calculated, and from them v_2 and $\bar{x}_n$. Equation 52 determines $\bar{x}_{n\text{A}}{}'$, from which $v_{2\text{A}}{}'$ may be evaluated according to eq 19. Equation 51 then gives $v_2{}'$. Substitution of results thus obtained in eq 20′ and 53 completes the calculation of η and y, which may be compared with the trial values.

For a highly ordered anisotropic phase appropriately considered to be ideal ($y = 1$), eq 1–44, 1, 24, and 44 yield

$$v_x = v_2'(1-p)^2 p^{-1}(1-pv_2')^{-1} x^3 c^x \tag{54}$$

where

$$c = p\exp[-(1-1/\bar{x}_n)v_2] \tag{55}$$

It follows that

$$v_2 = v_2'[(1-p)^2/p(1-pv_2')](c+4c^2+c^3)/(1-c)^4 \tag{56}$$

and

$$\bar{x}_n = (1+4c+c^2)/(1-c^2) \tag{57}$$

Equation 1–43 in this limiting case takes the form

$$(1-v_2')/(1-pv_2') = (1-v_2)\exp[(1-1/\bar{x}_n)v_2] \tag{58}$$

Given the value of p, solution of eq 55–58 yields v_2 and $\bar{x}_n$ for the incipient isotropic phase and v_2' for the anisotropic phase in which the solute conforms to the distribution specified by p.

6. Undiluted Systems. Trial calculations show y_{eq} to be less than unity in the absence of diluent for any $\bar{x}_n^0$ large enough to produce an anisotropic phase. Hence, $I_{0\mathrm{R}}$ and $I_{1\mathrm{R}}$ vanish and $I_{0\mathrm{A}}$ and $I_{1\mathrm{A}}$ given by eq 16 and 14, respectively, may be identified with I_0 and I_1 for the corresponding sums that extend from 1 to ∞. Taking $v_2 = v_2' = v_2^0 = 1$, we obtain from eq 13, 15, and 20′

$$\Phi = (y/e)^2(1-p)^2 I_1 \tag{59}$$

$$\bar{x}_n' = y\exp(2/y) = I_1/I_0 \tag{60}$$

$$\eta = 1 - 1/\bar{x}_n - (1-y^{-1})\exp(-2/y) \tag{61}$$

Substitution of eq 60 in eq 6 gives

$$1/\bar{x}_n = (1-p)\Phi^{-1} - (1-\Phi)\Phi^{-1}y^{-1}\exp(-2/y) \tag{62}$$

Given p, these equations may be solved by choosing trial values of Φ and y. Equations 61 and 62 yield η which, in conjunction with p, Φ, and y, permits I_1 and I_0 to be evaluated according to eq 14 and 16. Values of Φ and y may then be calculated from eq 59 and from eq 60 and 61, these to be compared with the trial values, etc. The quantities $\bar{x}_n$, y, and $\bar{x}_n'$ characterizing the coexisting phases are thus determined together with the relative quantities Φ and $1 - \Phi$ of the two phases.

The solutions at the limits $\Phi = 0$ and 1 are unique. The latter, obtained by substitution of $v_2 = 1$ in eq 40, is $p = 0.56714$, or $\bar{x}_n = 2.3102$, along with $y = 0$, $v_2' = 1$, and $\bar{x}_n' = \infty$; see eq 39, 42, and 43.

The unique solution in the limit $\Phi = 0$ may be deduced as follows. Equations 47 and 48 can be simplified by omission of their second terms, y being <1. Hence, eq 47, 48, and 50 yield

$$\bar{x}_n = (1+4a+a^2)(1-a^2)^{-1} \tag{63}$$

Substitution of eq 44 in eq 60 gives

$$1-p = y^{-1}\exp(-2/y) \tag{64}$$

which also follows directly from eq 19. Replacing η in eq 20′ by $\ln(p/a)$ according to the definition of a, substituting from eq 63 for $\bar{x}_n$, making the further substitutions $v_{2\mathrm{A}}' = v_2' = v_2 = 1$ and $\bar{x}_{n\mathrm{A}}' = \bar{x}_n' = (1-p)^{-1}$, and, finally, substituting from eq 64 for p, we obtain

$$\ln[1 - y^{-1}\exp(-2/y)] + (1-y^{-1})e^{-2/y} = 2a(a+2)(1+4a+a^2)^{-1} + \ln a \tag{65}$$

Similar substitutions in eq 49 yield

$$y^3 e^{-2}[y\exp(4/y) - \exp(2/y)] = (a+4a^2+a^3)(1-a)^{-4} \tag{66}$$

Simultaneous solution of eq 65 and 66 yields $a = 0.44424$ and $y = 0.58640$, from which one obtains $\bar{x}_n = 3.7056$, $p = 0.943690$, and $\bar{x}_n' = 17.7589$.

If the anisotropic phase is treated as ideal, then eq 23 and 24 reduce to

$$D = (1-\Phi)\Phi^{-1}/\bar{x}_n' = (1-\Phi)\Phi^{-1}I_0 I_1^{-1} \tag{67}$$

$$\eta^* = 1 - 1/\bar{x}_n \tag{68}$$

respectively, when $v_2 = v_2' = v_2^0 = 1$. Combination of eq 25 with 67 gives

$$\Phi = (1-p)^2 I_0 \tag{69}$$

Substitution of eq 67 and 69 in 33 yields

$$1/\bar{x}_n = (1-p)\Phi^{-1} - (1-\Phi)\Phi^{-1}/\bar{x}_n' = (1-p)\Phi^{-1} - D \tag{70}$$

Given p, these equations can be solved by first choosing trial values of D and η^*, then calculating I_0 and I_1 from eq 27 and 28, respectively, and $\bar{x}_n'$ from eq 26.

Results for $y = 1$ at the limit $\Phi = 1$ are identical with those for $y = y_{\mathrm{eq}}$; see above.

At the limit $\Phi = 0$, with $y = 1$, eq 55–57 yield for $v_2 = v_2' = 1$

$$\ln p = \ln c + 2c(2+c)/(1+4c+c^2) \tag{71}$$

and

$$p^{-1} = 1 + (1-c)^4/(c+4c^2+c^3) \tag{72}$$

Numerical solution of these equations gives $c = 0.44937$, $p = 0.936154$, $\bar{x}_n' = (1-p)^{-1} = 15.6627$, and $\bar{x}_n = 3.7584$. Thus, $\bar{x}_n$ for the incipient phase agrees closely with the value calculated for $y = y_{\mathrm{eq}}$, but $\bar{x}_n'$ is somewhat smaller than the value thus calculated.

Results of Numerical Calculations

Figure 1 shows distributions in the coexisting phases for $p = 0.875$ and $\Phi = 0.50$ calculated according to the equations and procedure given in section 2 above. The ordinates on the left are ratios f_x and f_x' of the quantities of x-mer in the respective phases to the total quantity of solute in both phases: i.e.,

$$f_x = \Phi v_x/v_2^0 \tag{73}$$

$$f_x' = (1-\Phi)v_x'/v_2^0 \tag{74}$$

Also shown is the sum of these quantities

$$f_x^0 = f_x + f_x' = v_x^0/v_2^0 \tag{75}$$

expressing the volume fraction of x-mer in the combined system of two phases. The right-hand ordinate scales the f_x' curve to the distribution v_x'/v_2' of x-mer within the solute present in the anisotropic phase.

Parameters deduced for this system following the procedure detailed in section 2 above are given in the second row of Table I, together with quantities characterizing the concentrations and distributions in the coexisting phases. Inasmuch as $y < 1$ in this instance, the distribution f_x' was calculated according to eq 12 for all species. Use of the relations given in section 3 on the premise that the anisotropic phase should be treated as ideal yields results that do not differ significantly from those shown in Figure 1 and summarized by the data in the second row of Table I.

The slight upturn in the distribution f_x' shown in Figure 1 as x approaches unity reflects the dominance of the term

Table I
Parameters Calculated for Coexisting Phases for p = 0.875

$1-\Phi$	η	y	v_2	v_2'	$\overline{x}_n$	$\overline{x}_n'$	$\overline{x}_w/\overline{x}_n$	$\overline{x}_w'/\overline{x}_n'$
0.776	0.7648	0.7193	1.000	1.000	3.855	11.599	1.411	1.528
0.500	0.6057	0.8857	0.7484	0.9519	5.006	15.102	1.477	1.389
0.100	0.3948	1.236	0.4689	0.8436	7.051	24.493	1.661	1.284
0.010	0.2963	1.372	0.3479	0.7958	7.857	37.294	1.815	1.264
10^{-25}	0.1569	0.640	0.1783	0.9577	8.000	361.1	1.875	1.156
0	0.1335	0	0.1526	1.000	8.000	∞	1.875	∞

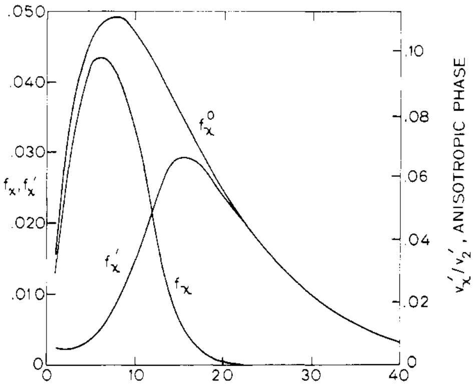

Figure 1. Partitioning of solute having the volume fraction distribution f_x^0 given by eq 1 with p = 0.875 between isotropic (f_x) and anisotropic (f_x') phases, where x is the axis ratio and $f_x + f_x' = f_x^0$. Calculations were carried out as described in the text for Φ = 0.50, i.e., for equal volumes of the two phases. The curve for f_x' when referred to the right-hand ordinate axis expresses the distribution within the anisotropic phase normalized to the total solute in that phase.

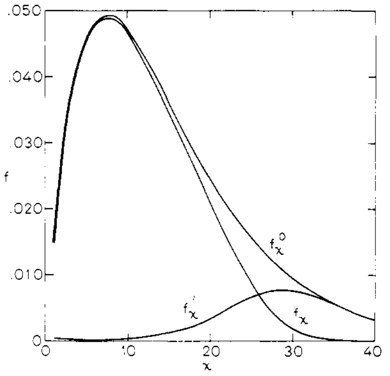

Figure 2. Partitioning of the solute distribution between the two phases for p = 0.875 and Φ = 0.90, i.e., for a volume ratio of 9:1 for isotropic and anisotropic phases, respectively. See legend to Figure 1.

$x^2 \exp(-\eta x)$ in the denominator of eq 12 when x is small (see also Figures 2 and 3). From a physical point of view, the adoption of the equilibrium value for y imposes an orientational constraint y/x that is less severe the smaller the value of x.[1] Hence, very short species are not strongly excluded from the anisotropic phase.

Marked disproportionation of species with low and high axis ratios between the respective phases is evident in Figure 1. This is reminiscent of the results presented in part 2 for solutes comprising two species. The distributions in the two phases are much narrower than the parent distribution. This is reflected in their respective weight-to-number average ratios, $\overline{x}_w/\overline{x}_n$ and $\overline{x}_w'/\overline{x}_n'$, given in Table I compared with $\overline{x}_w^0/\overline{x}_n^0$ = 1.875 for the parent distribution. Fractionation between the two phases is exceptionally efficient.

Corresponding results are shown in Figure 2 for p = 0.875 and Φ = 0.90, and in Figure 3 for p = 0.875 and Φ = 0.99; see also Table I. As the proportion $1 - \Phi$ of the anisotropic phase is decreased for the chosen value of p, the value of x demarcating species occurring preferentially in one phase from those preferring the other increases. As $1 - \Phi$ becomes very small, only the extremity of the distribution at large x is acquired by the anisotropic phase. The "cut-off" range increases as $1 - \Phi$ decreases.

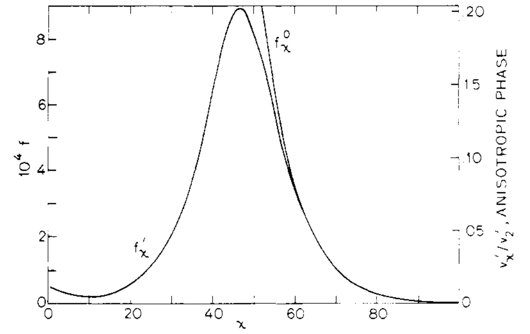

Figure 3. The distribution of species in the anisotropic phase for p = 0.875 and Φ = 0.99. See legend to Figure 1.

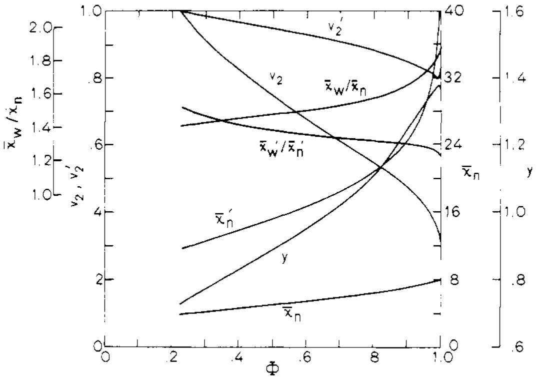

Figure 4. Characteristics of the phases in equilibrium for p = 0.875 as functions of the ratio Φ of the volume of the isotropic phase to the total volume.

The various quantities listed for illustration in Table I are plotted in Figure 4 as functions of Φ for p = 0.875. Convergence of the curves for v_2 and v_2' to unity at $\Phi \approx$ 0.224 signifies separation of the undiluted solute into two phases, their respective quantities being in the ratio $\Phi/(1 - \Phi)$. The number average length of the solute in the anisotropic phase is nearly three times that of the solute in the isotropic phase; see the first entry in Table I. Throughout the range of Φ discernible in Figure 4 both v_2 and v_2' decrease with Φ; i.e., dilution of the system as a whole, which requires the relative fraction Φ of the isotropic phase to increase, causes v_2' to decrease (except for $\Phi > \sim$0.993; see below). The rapid increase in $\overline{x}_n'$ with Φ reflects the selective retention of the largest species in the anisotropic phase as its relative amount $1 - \Phi$ decreases. The concurrent increase in $\overline{x}_n$ is a consequence of the increasing portion of the solute distribution acquired by the isotropic phase as Φ increases. Over the preponderance of the range y increases with Φ. The ratio $\overline{x}_w'/\overline{x}_n'$, which is indicative of the polydispersity of the solute in the anisotropic phase, diminishes monotonically with

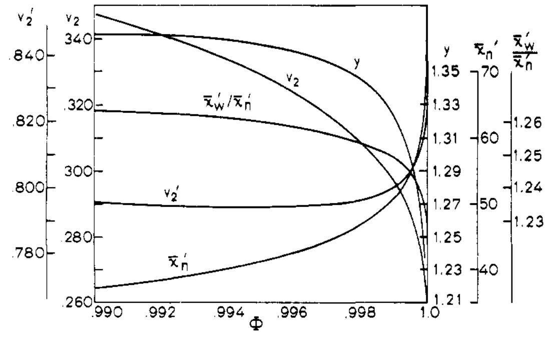

Figure 5. Enlargement of Figure 4 in the range Φ = 0.99–1.00.

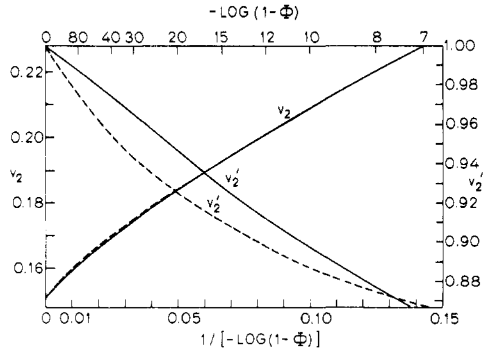

Figure 6. Plot of concentrations v_2 and v_2' in the coexisting phases against $[-\log(1-\Phi)]^{-1}$ in the range of very small values of 1 − Φ for $p = 0.875$. Solid curves were calculated with $y = y_{eq}$. The disorder index $y = y_{eq}$ is <1 for values of the abscissa <0.13. Dashed curves were calculated with $y = 1$ throughout the range of this plot.

decrease in the proportion of that phase according to the curve in Figure 4.

In Figure 5 the principal quantities appearing in Figure 4 are plotted against Φ in the range beyond 0.99. The trends of v_2' and y observed in Figure 4 and cited above reverse when Φ approaches unity; see Figure 5. Simultaneously, v_2 and $\bar{x}_w'/\bar{x}_n'$ exhibit accelerated decreases with Φ. The expanded scale of Figure 5 does not suffice, however, to delineate the ultimate courses of these functions as $\Phi \rightarrow 1$. Numerical calculations extending to $\Phi \approx 10^{-80}$ reveal an extremely protracted approach to the limiting values deduced in section 4 for Φ = 1.

For the purpose of displaying the peculiar behavior of these functions for unrealistically small 1 − Φ, we plot v_2 and v_2' against $[-\log(1-\Phi)]^{-1}$ for $p = 0.875$ in Figure 6. The choice of this quantity for the abscissa is quite arbitrary, apart from compliance with the requirement that it reach zero at Φ = 1. Values of $-\log(1-\Phi)$ are given along the upper margin. The solid curves represent results calculated in the foregoing manner. Inasmuch as $y = y_{eq}$ falls below unity in the vicinity of $1 - \Phi = 2 \times 10^{-8}$, calculations were performed also for an ideal anisotropic phase, the procedures presented in section 3 being followed for this purpose. Results of these calculations are shown by dashed lines. Both sets of results proceed smoothly to their common limits deduced in section 4 for Φ = 1. Values of v_2 calculated on the two bases differ imperceptibly except within the lower range of the abscissa. Even here the differences are very small. The corresponding curves for v_2' show a greater divergence. They intersect, as required, when $y = 1$. This occurs at $1 - \Phi = 2.1 \times 10^{-8}$.

The ratio $\bar{x}_w'/\bar{x}_n'$, not shown in Figure 6, decreases from a value of 1.264 at Φ = 0.99 (see Table I) to 1.1556 at $1 - \Phi = 10^{-25}$. Then, according to numerical calculations, it increases with further decrease in 1 − Φ, reaching 1.1934 at $1 - \Phi = 10^{-80}$. Analysis of the equations above leads to the conclusion that $\bar{x}_w'/\bar{x}_n'$ must increase without limit as Φ is further diminished. These deductions for extremely small Φ are, of course, of no physical relevance.

The phase volume ratio Φ required for reasonable approach to limiting values of the concentrations and other relevant quantities deduced analytically in section 4 obviously is unattainable in practice. Experiments on systems in biphasic equilibrium must necessarily be conducted therefore at concentrations v_2 considerably higher than those deduced above by solution of the relevant equations. Otherwise, the quantity of the anisotropic phase is far too small for observation and measurement. Incipient separation of an anisotropic phase should commence at $v_2 = 0.1526$ according to eq 40 for $p = 0.875$. As the calculations in Figures 5 and 6 show, a concentration v_2 nearly twice as great would be required to generate an anisotropic phase in quantity sufficient to meet the requirements of an experiment. It follows of course that the concentration for observed incipience of phase separation is ill-defined and its experimental determination may depend on the sensitivity of the method used.

Distribution curves for $p = 0.95$ (i.e., $\bar{x}_n^0 = 20$) and $\Phi = 0.50$ are shown in Figure 7. They reiterate the features revealed in Figure 1. The fractionation of species between the two phases is somewhat more efficient, however, for this distribution of species of higher average length. In Figure 8 we show the various quantities characterizing the two phases in equilibrium as a function of Φ for a solute having this distribution, specified by $p = 0.95$. The undiluted solute occurs as a single anisotropic phase in this instance, in contrast to the distribution with $p = 0.875$, i.e., for $\bar{x}_n^0 = 8$. An isotropic phase separates upon dilution, the extent of dilution required in this example being very small, as will be apparent from Figure 8.

At the opposite extreme, the emergence of an anisotropic phase with increase in the concentration v_2 is fraught with

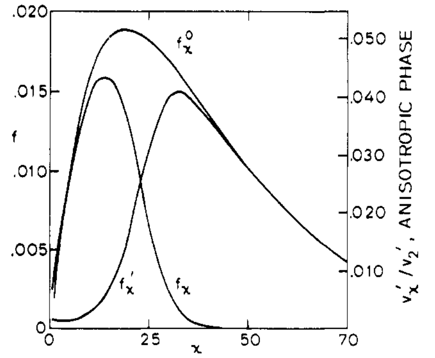

Figure 7. Partitioning of solute between phases for $p = 0.95$ (i.e., $\bar{x}_n^0 = 20$) and Φ = 0.50. See legend to Figure 1.

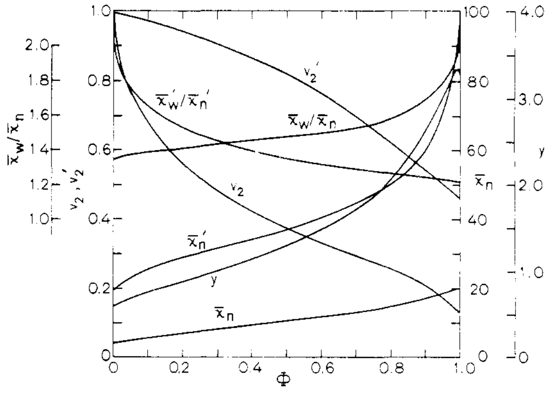

Figure 8. Characteristics of the phases in equilibrium for $p = 0.95$ as functions of the fraction Φ of isotropic phase.

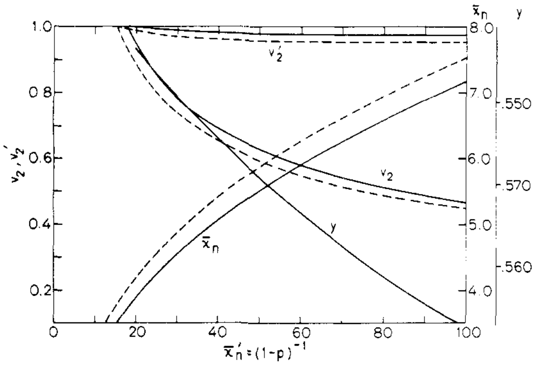

Figure 9. Concentration v_2 and average rod length $\bar{x}_n$ in the incipient isotropic phase ($\Phi = 0$) separating from an anisotropic phase of concentration v_2', plotted against the average rod length $\bar{x}_n'$ in the parent anisotropic phase. Also shown is the disorder index y. Solid curves were calculated with $y = y_{eq}$; dashed curves represent calculations with $y = 1$.

the same difficulties cited above for $p = 0.875$. Thus, for $p = 0.95$ a concentration $v_2 = 0.0540$ marks the point for incipient separation of an anisotropic phase from the solution according to eq 40. In order for this phase to occur in detectable quantity, however, a concentration on the order of $v_2 = 0.10$ would be required.

By contrast, the appearance of the isotropic phase upon dilution of the anisotropic phase comprising the undiluted solute with $\bar{x}_n = 20$ is well defined. This is indicated in Figure 8 by the small (but finite) inclination of the curve for v_2' at the limit $\Phi = 0$. Thus, the magnitude of $(d\Phi/dv_2')_{v_2'=0}$ is large, indicating abrupt emergence of the isotropic phase.

Values of v_2, v_2', y, and $\bar{x}_n$ at incipience of separation of an isotropic phase ($\Phi = 0$) are plotted in Figure 9 against the average axis ratio $\bar{x}_n'$ in the parent (anisotropic) phase. Solid curves were calculated by the procedure given in section 5 for $y = y_{eq}$. Dashed curves represent calculations for $y = 1$ carried out according to eq 55–58 of section 5. The parent anisotropic phase acquires little diluent and, consequently, y remains small. The concentration in the incipient isotropic phase decreases and $\bar{x}_n$ therein increases with increase in $\bar{x}_n'$. The limit $v_2 = v_2' = 1$ occurs at $\bar{x}_n' = (1 - p)^{-1} = 17.76$ according to the former of the two procedures (solid lines in Figure 9) and at 15.66 according to the latter method (dashed lines). Separation of an isotropic phase is incipient in absence of diluent at this point.

Calculations pertaining to phase equilibria in undiluted systems in which $\bar{x}_n^0$ for the material as a whole falls below the limit identified above are presented in Figure 10. Here, Φ, y, $\bar{x}_n$, and $\bar{x}_n'$ are plotted against $\bar{x}_n^0 = (1 - p)^{-1}$. Solid curves were calculated for $y = y_{eq}$ using eq 59–62. Dashed curves were calculated from eq 67–70 for $y = 1$. In a sense, Figure 10 is the logical extension of Figure 9 into the region where dilution is not required to render the system biphasic. The limiting point $\bar{x}_n^0 = (1 - p)^{-1} = 2.3102$ at which $v_2 = 1$ according to eq 40 is subject to the same ambiguities discussed above for $1 - \Phi = 0$ at larger values of $\bar{x}_n^0$ and, correspondingly, of p. The biphasic range for the undiluted distribution is broad. It commences at $\bar{x}_n^0 = 2.31$ (approximately, see above) and extends to $\bar{x}_n^0 = 17.76$ (calculated for $y = y_{eq}$). By way of comparison, an axis ratio $x = 6.70183$ is required for biphasic equilibrium in undiluted, monodisperse rods, according to theory.[4]

Discussion

According to theory[3,4] the biphasic region in the case of a monodisperse, rodlike solute should be quite narrow; for

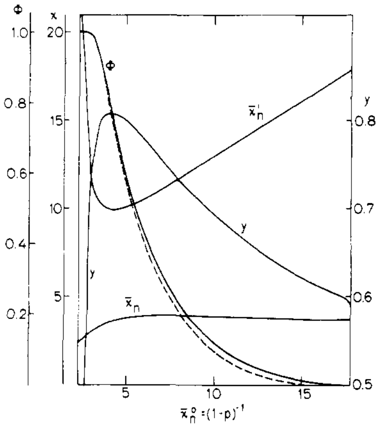

Figure 10. The fractional volume Φ of the isotropic phase plotted against the average rod length $\bar{x}_n^0$ for the system as a whole over the range within which it is predicted to be biphasic without dilution. Also shown are the average rod lengths $\bar{x}_n$ and $\bar{x}_n'$ in the isotropic and anisotropic phases, respectively, and the disorder index y in the latter. Solid curves calculated with $y = y_{eq}$; dashed curves are for $y = 1$.

$x > 20$, $v_2'/v_2 \approx 1.5^4$ (=1.5923 in the limit $x \to \infty$). Calculations presented in the preceding paper[2] for systems in which the solute comprises a binary mixture of rodlike particles differing in length show the immiscibility gap to be markedly broadened by addition of the second solute component. Corresponding effects are even more pronounced for a most probable distribution of solute species, according to the calculations presented here.

Consider, for example, the case $\bar{x}_n^0 = 20$. For a monodisperse solute with $x = 20$, the concentrations in the coexisting phases are $v_2 = 0.379$ and $v_2' = 0.540$, respectively. According to the calculations presented in Figure 8, the distribution with $\bar{x}_n^0 = 20$ ($p = 0.95$) should manifest measurable phase separation commencing at $v_2 \approx 0.1$, i.e., at a much lower concentration than for the monodisperse solute. However, total conversion to the anisotropic phase is not completed until $v_2^0 = v_2' \approx 0.99$, which is substantially greater than v_2' for the monodisperse solute.

The physical basis for this broadening of the biphasic region is implicit in the selective transferral of larger species to the anisotropic phase. Thus, the solute in the incipient anisotropic phase at $(1 - \Phi) << 1$ comprises species with x considerably greater than $\bar{x}_n^0$. As $\Phi \to 0$, the vanishing isotropic phase retains only species with $x << x_n^0$ (see Figure 8). For reasons unexplained, experiments on phase equilibria in solutions of polydisperse α-helical polypeptides appear to be at variance with this elementary prediction.[5,6]

Equilibrium with an isotropic phase containing an arbitrarily specified distribution of solute species requires a conjugate anisotropic phase having the composition deduced for the incipient anisotropic phase. The composition and distribution in this latter phase are unique to the distribution specified for the isotropic phase. The required concentration v_2 for the isotropic phase is likewise uniquely determined by the specified distribution.

For biphasic equilibrium with a "most probable" distribution in the isotropic phase, the concentration v_2 in that phase is given by eq 40. The conjugate anisotropic phase is characterized by $v_2' = 1$, $\bar{x}_n' = \infty$, and $y = 0$ (or 1); i.e., this phase consists of perfectly ordered species of infinite length, according to the analysis presented. These conditions apply regardless of the average axis ratio $\bar{x}_n = (1 - p)^{-1}$ in the isotropic phase, provided that $\bar{x}_n > 2.3102$. If the anisotropic phase contains solvent, is finitely disoriented, or consists of rods of finite lengths, then, strictly speaking, it is disqualified for coexistence in equilibrium with an isotropic phase in which the solute comprises rods having a most probable distribution of lengths. This distribution must be vitiated through selective transfer of species between the two phases if equilibrium is to be established.

The foregoing conditions that follow formally from the solution of the equations applicable at equilibrium are relaxed considerably when adapted to real systems. As shown above, formation of a measurable quantity of the anisotropic phase from a finite isotropic phase requires a concentration v_2 substantially higher than that given by eq 40. Also, v_2' falls appreciably below unity and a finite degree of disorder may occur. The penultimate row of Table I is illustrative. Nevertheless, generation of an anisotropic phase in significant quantity from an isotropic phase in which, prior to separation of that phase, the solute composition is described by the most probable distribution removes a significant fraction of the largest species from that distribution. The higher range of the distribution consequently suffers depletion.

It is interesting to reflect on the consequences of molecular exchange, facilitated perhaps by the action of a catalyst, in a system in biphasic equilibrium. Assume for simplicity that the species of size x is a polymer M_x comprising x units joined in rigid, rodlike arrangement. Let the chemical potential of structural units be fixed (as in an open chemical system). Random interchange of units between species under the aegis of the catalyst mobilizes the array of processes typified by

$$M_{x_1} + M_{x_2} \rightleftarrows M_{x_1+x_2}$$

For purposes of exposition, we assume the catalyst to be effective only in the isotropic phase. That this arbitrary restriction can have no effect on the final state of equilibrium is assured by the second law of thermodynamics. The condition of equal reactivity, which may be presumed to hold in the isotropic phase (and in the anisotropic phase as well), requires generation of the most probable distribution with p (and $\bar{x}_n$) determined by the (fixed) chemical potentials, and maintenance of that distribution at equilibrium.[7] But the coexisting anisotropic phase will sequester the larger species. Replenishment of these species through chemical exchange perpetuates transfer to the ordered phase. It follows that the polymer must ultimately be transferred in its entirety to the anisotropic phase for any sustained concentration v_2 sufficiently above the hypothetical limit given by eq 40. For v_2 not greatly in excess of this limit, the anisotropic phase should be concentrated and highly ordered with $\bar{x}_n'$ very large.

The combination of a chemically mobile aggregation process potentially capable of yielding highly anisometric particles and phase separation provides a singularly simple mechanism for self-organization with possible relevancy to biological systems.[8]

It should be noted that, in absence of diluent, complete conversion to the very long rods comprising an anisotropic phase is predicted for any value of p (determined by the chemical potentials in the chemically mobile system considered; see above) which exceeds $p = 0.56714$, this being the solution of eq 40 for $v_2 = 1$. The corresponding average rod length (in absence of separation of an anisotropic phase) is only $\bar{x}_n = 2.3102$. Thus, the tendency for concatenation need not be large for complete conversion, in the presence of a catalyst, to a highly ordered phase.

The theory and calculations presented here and in the two preceding papers rest entirely on the shape anisotropy of rodlike particles. Interparticle attractions are deliberately disregarded altogether. The extent to which such interactions may affect the equilibria remains to be investigated. It is significantly of interest, at the very least, that so much follows from asymmetry of shape alone, without appeal to other factors.

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References and Notes

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(2) A. Abe and P. J. Flory, *Macromolecules*, companion paper in this issue, part 2.

(3) L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).

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(6) E. L. Wee and W. G. Miller, *J. Phys. Chem.*, **75**, 1446 (1971); W. G. Miller, J. H. Rai, and E. L. Wee, "Liquid Crystals and Ordered Fluids", Vol. 2, J. F. Johnson and R. S. Porter, Ed., Plenum Publishing Corp., New York, N.Y., 1974, pp 243-255.

(7) That maximization of the partition function for the mixture of linear polymer species M_x in an isotropic phase subject to constancy of $\sum n_x = n_2$ and of $\sum x n_x$ leads to the most probable distribution is well known. The same result follows from the partition function for an anisotropic phase given by eq 1-19. Hence, interchange equilibration in an anisotropic phase must likewise yield a most probable distribution. Exchange of species between two such phases leads to the consequences discussed in the text.

(8) The authors are indebted to Dr. L. Peller for bringing this possible application of the theory to their attention, and for an illuminating discourse on this subject.