(8) Viovy, J. L.; Monnerie, L.; Tassin, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2427.
(9) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(10) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(11) Viovy, J. L. *J. Phys. (Paris)* **1985**, *46*, 847.
(12) Thirion, P.; Tassin, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2097.
(13) Tassin, J. F.; Thirion, P.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2109.
(14) Tassin, J. F. Thèse doctorat d'état, Univ. Paris VI, 1986.
(15) Tassin, J. F.; Monnerie, L.; Fetters, L. J. *Polym. Bull.* **1986**, *15*, 165.
(16) Fajolle, R.; Tassin, J. F.; Sergot, P.; Pambrun, C.; Monnerie, L. *Polymer* **1983**, *24*, 379.
(17) Lefebvre, D.; Jasse, B.; Monnerie, L. *Polymer* **1983**, *24*, 1240.
(18) Plazeck, D. J. *J. Phys. Chem.* **1965**, *69*, 3480.
(19) Muller, R.; Froelich, D. *Polymer* **1985**, *26*, 1477.
(20) Curtiss, C. F.; Bird, R. B. *J. Chem. Phys.* **1981**, *74*, 2016, 2026.
(21) Lawrey, B. D.; Prud'homme, R. K.; Koberstein, J. T. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 203.
(22) Treloar, L. R. G. *Trans. Faraday Soc.* **1947**, *43*, 277.
(23) Kuhn, W.; Grun, F. *Koll. Zeit.* **1942**, *101*, 248.
(24) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(25) Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722.
(26) Boué, F.; Nierlich, M.; Jannink, G.; Ball, R. C. *J. Phys. (Paris)* **1982**, *43*, 137.
(27) Monfort, J. P.; Marin, G.; Monge, P. *Macromolecules* **1984**, *17*, 1551.
(28) Tobolsky, A. V.; Aklonis, J. J.; Akovali, G. *J. Chem. Phys.* **1965**, *42*, 723.
(29) Retting, W. *Colloid Polym. Sci.* **1979**, *257*, 689.
(30) Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer Verlag: Berlin, 1983.
(31) Tobolsky, A. V.; Aklonis, J. J. *J. Phys. Chem.* **1964**, *68*, 1970.
(32) Aklonis, J. J.; Tobolsky, A. V. *J. Appl. Phys.* **1965**, *36*, 3483.
(33) Aklonis, J. J.; Rele, V. B. *J. Polym. Sci., Symp.* **1974**, *46*, 127.
(34) Bastide, J.; Herz, J.; Boué, F. *J. Phys. (Paris)* **1985**, *46*, 1967.

Statistical Thermodynamics of Mixtures of Rodlike Particles. Surface Tension and the Most Probable Distribution

Randall S. Frost

1045 Catalina Dr., Apt. 13, Livermore, California 94550. *Received September 18, 1987; Revised Manuscript Received December 29, 1987*

ABSTRACT: The surface tension in an anisotropic monolayer is investigated for athermal mixtures in which the solute comprises rodlike molecules having the familiar most probable, or Flory, 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. Preferential partitioning of lower and higher species between isotropic and anisotropic phases, respectively, may favor the formation of an anisotropic surface layer of solute particles with considerable lowering of surface tension. Over the range that the undiluted polydisperse solute is biphasic, however, self-ordering of the rods in the surface layer cannot in itself bring about a lowering of surface tension. We also find that the alteration of surface tension due to the formation of a surface layer of anisotropic material that has separated out of a parent isotropic phase (in which the solute retains the foregoing distribution) does not occur spontaneously but rather depends on the presence of a finite amount of ordered material in the mixture. In the limit that the anisotropic phase retains the parent distribution, there exists a range of $(1 - p)^{-1}$ between ~18 and 42 over which theory predicts the formation of an incipient isotropic phase at the surface; at larger values of $(1 - p)^{-1}$ theory favors the presence of an anisotropic layer at the surface.

Introduction

This paper treats the surface tension of an athermal mixture of rodlike particles having a most probable, or Flory, distribution of axial ratios and partitioned into isotropic and anisotropic phases. As in the previously published papers,[1-3] exchange interactions between solute particles are assumed to be null, and only spaciogeometric requirements are considered.

A theory first proposed in 1941 by Flory[4] introduced the quasicrystalline lattice theory to describe the statistical thermodynamics of macromolecules and solvent molecules in equilibrium. According to the theory, solvent molecules (type 1) occupy one lattice site, while macromolecules (type 2) occupy x contiguous lattice sites (x-mers). Finding the number of ways of arranging the molecules in space, by taking into account molecular volumes and shapes and calculating the entropy of mixing, is found by counting the number of geometrical configurations accessible to each type of molecule on the lattice. Then, by determining the average number of contacts between molecular species, one can obtain the configurational energy and, finally, formulate the statistical mechanics of the solution.

In the limit that the volume fractions of solvent and solute molecules in a monolayer parallel to a surface in the liquid are nearly the same as their respective volume fractions in the liquid, it can be shown from the theoretical work of Prigogine,[5] which in turn was based upon Flory's pioneering quasilattice studies, that the surface tension s may be formulated as follows:

$$s = (s_1 v_1{}^{\mathrm{l}} + s_x v_2{}^{\mathrm{l}}) + (RT/a)[v_1{}^{\mathrm{l}} \ln (v_1{}^{\mathrm{m}}/v_1{}^{\mathrm{l}}) + v_2{}^{\mathrm{l}} x^{-1} \ln (v_2{}^{\mathrm{m}}/v_2{}^{\mathrm{l}}) + (x - 1)(v_2{}^{\mathrm{m}} - v_2{}^{\mathrm{l}})/x] \quad (1)$$

Or, to the degree of approximation assumed in this paper (cf. eq 10–17)

$$s \approx s_1 v_1 + s_x v_2 - a x v_1 v_2 (s_x - s_1)^2 / 2RT(v_1 + x v_2) \quad (2)$$

where superscripts l and m denote liquid and monolayer, respectively. Here, s_1 and s_x are the surface tensions of undiluted solvent and solute, respectively, v_1 and v_2 are the volume fractions of solvent and solute in the liquid, the parameter a is a constant corresponding to the molar surface area of a solvent molecule, and RT is the product of the gas constant and the absolute temperature.

Monodisperse Case

Although Prigogine[6] attempted to calculate the surface tension of rigid *rodlike* molecules as early as 1950 using Flory's quasilattice model, his approach was limited by the inability of the quasilattice model, as originally formulated, to adequately represent the geometric constraints imposed

0024-9297/88/2221-1854$01.50/0

by placing the rodlike particles on a lattice.

In 1956, Flory considered the problem of phase separation[1] in monodisperse rigid-rod solutions by modifying the original lattice theory. For these mixtures, separation of the particles into an isotropic phase and a somewhat more concentrated anisotropic phase was shown to occur solely as a consequence of particle asymmetry, unassisted by an energy term. Our starting point in formulating an expression for the surface tension in such rigid-rod systems will be to consider the chemical potentials of the molecules in the two phases, obtained by taking the appropriate derivatives of the combinatory partition function.

In the solvent, the chemical potential is[1]

$$(\mu_1^{\mathrm{l}} - \mu_1^{0,\mathrm{l}})/RT = \ln (1 - v_2^{\mathrm{l}}) + 2/y + (y - 1)v_2^{\mathrm{l}}/x \quad (3)$$

whereas in the solute it is

$$(\mu_2^{\mathrm{l}} - \mu_2^{0,\mathrm{l}})/RT = \ln v_2^{\mathrm{l}} + (y - 1)v_2^{\mathrm{l}} + 2 - \ln y^2 - \ln x \quad (4)$$

Here, the parameter y is an orientation factor that reflects the alignment of a particle. Specifically, the orientation of a rodlike x-mer making an angle θ with the domain axis of the lattice is represented by assuming there exist $y = x \sin \theta$ submolecules, each parallel to the domain axis. The superscript l indicates that these equations pertain to the liquid, as opposed to the surface monolayer, which will now be considered.

It follows from thermodynamic arguments that the chemical potentials in the monolayer will be identical with those in the liquid except for the presence of terms proportional to sa_i, where s is the surface tension and a_i is the molar surface area.[5,6] The chemical potential in the solvent becomes[2,7]

$$(\mu_1^{\mathrm{m}} - \mu_1^{0,\mathrm{m}})/RT = \ln (1 - v_2^{\mathrm{m}}) + 2/y + (y - 1)v_2^{\mathrm{m}}/x - sa/RT \quad (5)$$

and in the solute

$$(\mu_2^{\mathrm{m}} - \mu_2^{0,\mathrm{m}})/RT = \ln v_2^{\mathrm{m}} + (y - 1)v_2^{\mathrm{m}} + 2 - \ln y^2 - \ln x - sxa/RT \quad (6)$$

Here, the superscript m has been introduced to differentiate these equations for the monolayer from those describing the liquid. The parameter a retains its earlier meaning.

Equating the chemical potentials at the surface to those in the liquid provides us with two expressions for s. These are

$$s = s_1 - RT[x \ln \{(1 - v_2^{\mathrm{m}})/(1 - v_2^{\mathrm{l}})\} + (y - 1)(v_2^{\mathrm{m}} - v_2^{\mathrm{l}})]/ax \quad (7)$$

$$s = s_x - RT[x \ln (v_2^{\mathrm{m}}/v_2^{\mathrm{l}}) + (y - 1)(v_2^{\mathrm{m}} - v_2^{\mathrm{l}})]/ax \quad (8)$$

where $s_1 = (\mu_1^{0,\mathrm{m}} - \mu_1^{0,\mathrm{l}})/a$ and $s_x = (\mu_2^{0,\mathrm{m}} - \mu_2^{0,\mathrm{l}})/ax$ by definition.

Equations 7 and 8 can be written in an alternate form if we first subtract one from the other, thus obtaining an equation that relates the liquid and surface compositions:

$$v_1^{\mathrm{m}}/v_1^{\mathrm{l}} = (v_2^{\mathrm{m}}/v_2^{\mathrm{l}})^{1/x} \exp[(s_1 - s_x)a/RT] \quad (9)$$

Or, we can multiply eq 7 and 8 by v_1^{l} and v_2^{l} and then add to get

$$s = (s_1v_1^{\mathrm{l}} + s_2v_2^{\mathrm{l}}) + (RT/a)[v_1^{\mathrm{l}} \ln (v_1^{\mathrm{m}}/v_1^{\mathrm{l}}) + v_2^{\mathrm{l}}x^{-1} \ln (v_2^{\mathrm{m}}/v_2^{\mathrm{l}}) + (y - 1)(v_2^{\mathrm{m}} - v_2^{\mathrm{l}})/x] \quad (10)$$

which may be compared with eq 1 for the surface tension corresponding to a monolayer of isotropic molecules. Equations 1 and 10 are identical except that $x - 1$ in eq 1 has been replaced by $y - 1$ in eq 10. Of course, in the limit of random alignment $y = x$, and the two expressions become identical.

Unfortunately it is not possible to solve eq 9 algebraically for the surface compositions or to subsequently solve eq 10 to obtain an explicit expression for s in terms of v_1^{l} and v_2^{l}, except in trivial cases. We can, however, temporarily ignore the term in eq 10 that accounts for adsorption effects. Then to a crude approximation the surface tension is seen to vary linearly with volume fraction, i.e.

$$s \approx s_1v_1^{\mathrm{l}} + s_xv_2^{\mathrm{l}} \quad (11)$$

Requiring that $v_1^{\mathrm{m}} - v_1^{\mathrm{l}}$ and $v_2^{\mathrm{m}} - v_2^{\mathrm{l}}$ be small is equivalent to requiring that the dimensionless quantity $(s_x - s_1)a/RT$ be small compared to unity. In this limit the terms in eq 10 can be evaluated approximately. Proceeding along lines taken by Prigogine,[5] we write

$$v_1^{\mathrm{m}} = v_1^{\mathrm{l}} + v_1^{\mathrm{l}}v_2^{\mathrm{l}}\Delta \quad (12)$$

$$v_2^{\mathrm{m}} = v_2^{\mathrm{l}} - v_1^{\mathrm{l}}v_2^{\mathrm{l}}\Delta \quad (13)$$

where the parameter Δ, which is a small quantity that tends to 0 as $(v_2 - v_1)/RT$ approaches the same limit, can be evaluated from eq 9. Equations 12 and 13 have been written so that $v_1^{\mathrm{m}} = 0$ when $v_1^{\mathrm{l}} = 0$ and $v_1^{\mathrm{m}} = 1$ when $v_1^{\mathrm{l}} = 1$. Substituting for v_1^{m} and v_2^{m} by using eq 12 and 13 into eq 10 and expanding give

$$s \approx (s_1v_1^{\mathrm{l}} + s_2v_2^{\mathrm{l}}) + (RT/a)[v_1^{\mathrm{l}} \ln (1 + v_2^{\mathrm{l}}\Delta) + v_2^{\mathrm{l}}x^{-1} \ln (1 - v_1^{\mathrm{l}}\Delta) + (y - 1)(v_1^{\mathrm{l}}v_2^{\mathrm{l}}\Delta/x)] \quad (14)$$

Further expansion yields

$$s \approx (s_1v_1^{\mathrm{l}} + s_2v_2^{\mathrm{l}}) + (RT/a)(v_1^{\mathrm{l}}v_2^{\mathrm{l}})\{\Delta(1 - y/x) - (v_2^{\mathrm{l}} + v_1^{\mathrm{l}}/x)\Delta^2/2\} \quad (15)$$

The parameter Δ is evaluated by substituting from eq 12 and 13 into eq 9 and keeping only first-order terms in $(s_x - s_1)a/RT$. In this manner, we obtain

$$\Delta \approx (s_1 - s_x)a/RT(v_2^{\mathrm{l}} + v_1^{\mathrm{l}}/x) \quad (16)$$

The surface tension is easily evaluated by substituting eq 16 into eq 14 and cancelling like terms, i.e.

$$s \approx (s_1v_1^{\mathrm{l}} + s_2v_2^{\mathrm{l}}) + (v_1^{\mathrm{l}}v_2^{\mathrm{l}})(1 - y/x)(s_x - s_1)/(v_2^{\mathrm{l}} + v_1^{\mathrm{l}}/x) - [xv_1^{\mathrm{l}}v_2^{\mathrm{l}}(s_x - s_1)^2a/((v_1^{\mathrm{l}} + xv_2^{\mathrm{l}})RT)] \quad (17)$$

Equation 17, except for the presence of a first-order term in $s_x - s_1$, is identical with the expression one would obtain for isotropic solutions by expanding eq 1 and making the same approximations that led to eq 17. The first-order term vanishes in the limit where $y = x$, corresponding to complete disorder, in which case the two approximations are equivalent.

Polydispersity—The Most Probable Distribution[1-3]

In this section, we extend the lattice model to include polydisperse mixtures, such as are normally encountered in real systems. The systems considered are mixtures of rodlike particles with differing axis ratios x that are dispersed in a solvent. As before, we assume the rods to have identical diameters and their lengths to be variable. The solvent is taken to be isodiametric with its diameter equal to the mean thickness of the rods. Hence $x_{\mathrm{solvent}} = 1$. A solute segment is defined as the portion thereof having the same volume as a molecule of the solvent and hence being geometrically equivalent to the solvent molecule. Thus x is both the axis ratio and the number of segments constituting the solute molecule.

Again we consider a liquid-crystalline domain, or phase, in which the solute particles are preferentially oriented with respect to the cylindrical axis of the domain. As was shown,[2,3] the particles thus oriented may include only the larger species for which x exceeds some lower bound, smaller members of the distribution of species being randomly distributed over solid angle.

Following Flory and Abe,[2] we have for the chemical potential of the isotropic solvent

$$(\mu_1^{l} - \mu_2^{l,0})/RT = \ln(1 - v_2^{l}) + 2/y + v_{2r}^{l}(1 - 1/x_{nr}) + v_{2a}^{l}(y - 1)/x_{na} \tag{18}$$

For the solute in the anisotropic phase, the expressions are

$$(\mu_x^{l} - \mu_x^{l,0})/RT = \ln(v_x^{l}/x) + 2x/y - \ln x^2 + xv_{2r}^{l}(1 - 1/x_{nr}) + xv_{2a}^{l}(y - 1)/x_{na}; \quad x \le y \tag{19}$$

$$(\mu_x^{l} - \mu_x^{l,0})/RT = \ln(v_x^{l}/x) + 2 - \ln y^2 + xv_{2r}^{l}(1 - 1/x_{nr}) + xv_{2a}^{l}(y - 1)/x_{na}; \quad x > y \tag{20}$$

Here, the parameters v_{2r}, v_{2a}, x_{nr}, and x_{na} represent the solute volume fractions and number average axial ratios corresponding to randomly oriented (subscript r) and ordered (subscript a) solute species in the anisotropic phase.

In an anisotropic monolayer, the equivalent chemical potentials are

$$(\mu_1^{m} - \mu_2^{m,0})/RT = \ln(1 - v_2^{m}) + 2/y + v_{2r}^{m}(1 - 1/x_{nr}) + v_{2a}^{m}(y - 1)/x_{na} - sa/RT \tag{21}$$

$$(\mu_x^{m} - \mu_x^{m,0})/RT = \ln(v_x^{m}/x) + 2x/y - \ln x^2 + xv_{2r}^{m}(1 - 1/x_{nr}) + xv_{2a}^{m}(y - 1)/x_{na} - sxa/RT; \quad x \le y \tag{22}$$

$$(\mu_x^{m} - \mu_x^{m,0})/RT = \ln(v_x^{m}/x) + 2 - \ln y^2 + xv_{2r}^{m}(1 - 1/x_{nr}) + xv_{2a}^{m}(y - 1)/x_{na} - sxa/RT; \quad x > y \tag{23}$$

Equating the chemical potential for the solvent molecules in the liquid to that for the monolayer and then combining terms yield the following expression for s:

$$s = (\mu_1^{0,m} - \mu_1^{0,l})/a + (RT/a)\{\ln(v_1^{m}/v_1^{l}) + (y - 1) \times (v_{2a}^{m} - v_{2a}^{l})/x_{na} + (v_{2r}^{m} - v_{2r}^{l})(1 - 1/x_{nr})\} \tag{24}$$

Similarly, equating solute chemical potentials gives

$$s = (\mu_x^{0,m} - \mu_x^{0,l})/ax + (RT/a)[\ln(v_x^{m}/v_x^{l})^{1/x} + (y - 1)(v_{2a}^{m} - v_{2a}^{l})/x_{na} + (v_{2r}^{m} - v_{2r}^{l})(1 - 1/x_{nr})] \tag{25}$$

Upon multiplying eq 24 by v_1^{l} and eq 25 by v_2^{l}, we have

$$sv_1^{l} = s_1v_1^{l} + (RTv_1^{l}/a)\{\ln(v_1^{m}/v_1^{l}) + \beta\} \tag{26}$$

$$sv_2^{l} = s_xv_2^{l} + (RTv_2^{l}/a)\{\ln(v_x^{m}/v_x^{l}) + \beta\} \tag{27}$$

where

$$s_1 \equiv (\mu_1^{0,m} - \mu_1^{0,l})/a \tag{28}$$

$$s_x \equiv (\mu_x^{0,m} - \mu_x^{0,l})/ax \tag{29}$$

$$\beta \equiv (y - 1)(v_{2a}^{m} - v_{2a}^{l})/x_{na} + (v_{2r}^{m} - v_{2r}^{l})(1 - 1/x_{nr}) \tag{30}$$

Combining eq 26 and 27 to obtain

$$s = (s_1v_1^{l} + s_xv_x^{l}) + (RT/a)\{v_1^{l}\ln(v_1^{m}/v_1^{l}) + v_2^{l}\ln(v_x^{m}/v_x^{l})^{1/x} + \beta\} \tag{31}$$

and then writing

$$v_1^{m} \approx v_1^{l} + v_1^{l}v_2^{l}\Delta$$

$$v_x^{m} \approx v_x^{l} - v_1^{l}v_x^{l}\Delta$$

$$v_{2a}^{m} \approx v_{2a}^{l} - v_1^{l}v_{2a}^{l}\Delta$$

$$v_{2r}^{m} \approx v_{2r}^{l} - v_1^{l}v_{2r}^{l}\Delta$$

in close analogy to the approach taken for monodispersity, we can make the appropriate substitutions into eq 31 and perform the requisite algebra to obtain

$$s = (s_1v_1^{l} + s_xv_x^{l}) + (RT/a)(v_1^{l}v_2^{l})\{\Delta(1 - (y - 1) \times (v_{2a}^{l}/x_{na}v_2^{l}) - 1/x - (x_{nr} - 1)v_{2r}^{l}/x_{nr}v_2^{l}) - (v_2^{l} + v_1^{l}/x)\Delta^2/2\} \tag{32}$$

An expression for the polydisperse solution, analogous to eq 9 for the monodisperse one, is obtained by manipulating eq 24 and 25 to give

$$v_1^{m}/v_1^{l} = (v_x^{m}/v_x^{l})^{1/x}\exp[(s_x - s_1)a/RT] \tag{33}$$

Once again making use of the approximation $v_x^{m} \approx v_x^{l} - v_1^{l}v_x^{l}\Delta$, we can substitute into eq 33 and then expand terms on the right. Keeping only first-order terms in Δ and in $(s_x - s_1)a/RT$ allows us to write

$$\Delta \approx (s_x - s_1)a/RT(v_2^{l} + v_1^{l}/x) \tag{34}$$

Finally, substituting eq 34 into eq 32 yields the desired expression for the surface tension:

$$s \approx (s_1v_1^{l} + s_xv_2^{l}) + (s_x - s_1)(v_1^{l}v_2^{l})[1 - 1/x - (y - 1) \times (v_{2a}^{l}/x_{na}{}^{l}v_2^{l}) - [(x_{nr} - 1)v_{2r}^{l}/x_{nr}v_2^{l}]/(v_2^{l} + v_1^{l}/x)] - axv_1^{l}v_2^{l}(s_x - s_1)^2/(2RT(v_1^{l} + xv_2^{l})) \tag{35}$$

Note that eq 35 is of the same form as eq 17, derived for monodisperse solutions, i.e., both eq 17 and 35 can be written

$$s \approx (s_1v_1^{l} + s_xv_2^{l}) + a(s_x - s_1) - b(s_x - s_1)^2 \tag{36}$$

where a and b are dispersity-specific coefficients. Note also that the coefficient of $(s_x - s_1)^2$ in eq 35 (corresponding to b in eq 36) is identical with the term appearing in the expression for the surface tension of isotropic molecules (see eq 2) and is not in any way peculiar to the rigid-rod model. Aside from noting that this coefficient, whose temperature dependence is in qualitative accord with behavior in simple molecular solutions, reappears in the surface tension expression for rigid rods, we will not consider it in this paper. Rather, we will focus our attention on the coefficient of $(s_x - s_1)$, which arises from self-ordering of the rigid rods and does not have a corresponding term in eq 2. The coefficient can be evaluated exactly by using the computational methods described previously.[3]

Results of Numerical Calculations

In this section, we evaluate numerically the effects of self-ordering in an anisotropic monolayer at the surface of a polydisperse solution of rigid rods. Specifically, we consider surface tension effects for most probable distributions of rigid-rod axial ratios.

To evaluate eq 35, we equated chemical potentials corresponding to the solvent and solute particles in an anisotropic monolayer to the chemical potentials describing the anisotropic phase in equilibrium with an isotropic phase in the liquid. As we have noted, phase separation in polydisperse rigid rod solutions was earlier described by Flory and Abe[2] and investigated numerically for a most probable distribution of axial ratios by Flory and this author[3] to yield values of the parameters required to explicitly evaluate the coefficient of $(s_x - s_1)$ in eq 35 for specific values of most probable axial ratio $x_n^0 = (1 - p)^{-1}$ and relative volume of isotropic phase ϕ. A complete analysis using eq 35 and taking into account system-specific variations in molar surface area and temperature is beyond the scope of the present paper.

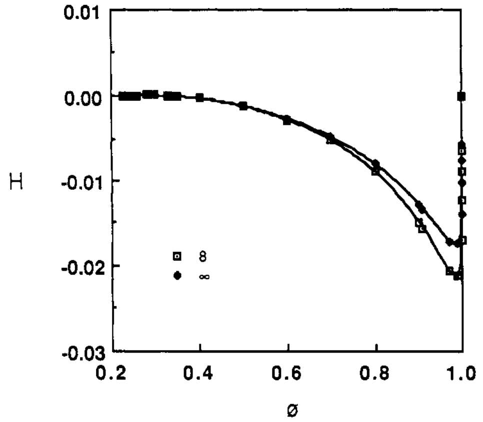

Figure 1. Component H (defined in eq 37) of surface tension directly attributable to self-ordering in a surface monolayer of anisotropic material that is in equilibrium with a biphasic solution of rigid rods for a most probable distribution of axial ratios having $x_n^0 = 8$. The parameter H, which has been evaluated at two axial ratios ($x = x_n^0 = 8$ and $x = \infty$) shows only slight variation with x over this range. Note the rapid variation of H with ϕ in the vicinity of $\phi \approx 0.99$.

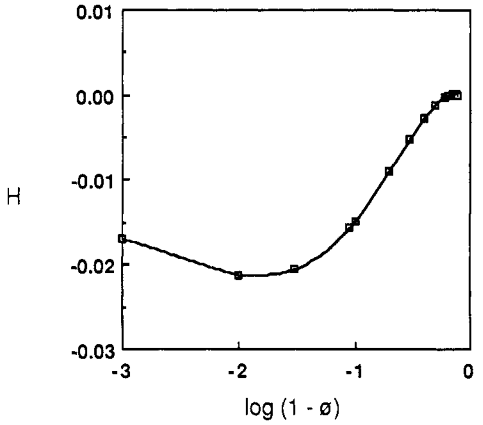

Figure 2. Self-ordering component H of surface tension shown as a semi-log plot of H against log $(1-\phi)$ for $x_n^0 = 8$. In the limit that log $(1-\phi)$ goes to $-\infty$, that is to say, as ϕ goes to 1, which corresponds to a purely isotropic solution in which the solute species retains a most probable distribution of axial ratios, H goes to 0. The upper bound on log $(1-\phi)$ occurs at $\phi \approx 0.224$, at which point $v_2 = 1$ and we also have $H = 0$. The approach of H to 0 in this region is shown in Figure 3.

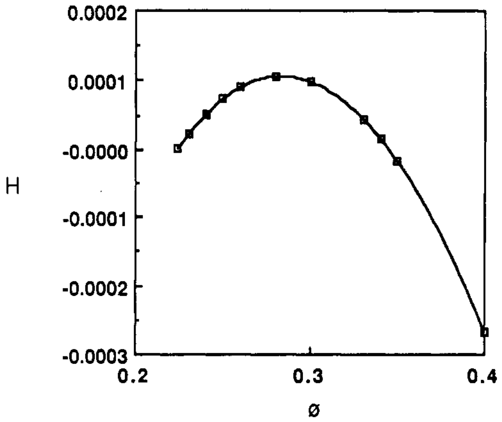

Figure 3. Self-ordering component H of surface tension for $x_n^0 = 8$ near the lower bound of ϕ (the axes of Figure 1 have been expanded vertically and horizontally). Note that in this region, H assumes positive values, resulting in a lower surface tension for the isotropic phase than for the anisotropic surface layer.

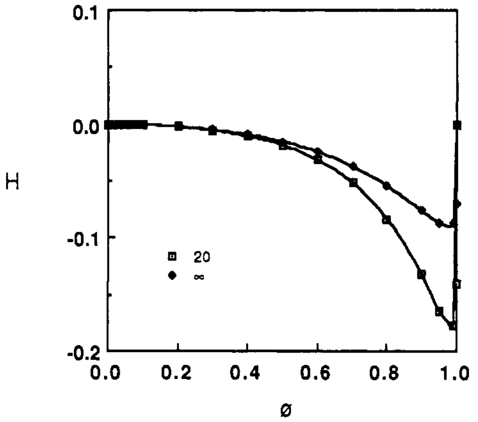

Figure 4. Self-ordering component H of surface tension for $x_n^0 = 20$, plotted in the same manner as in Figure 1 for $x_n^0 = 8$. In this case, biphasic equilibria extend over the range of $0 \le \phi \le 1$. Again, the parameter H has been evaluated at two axial ratios ($x = x_n^0 = 20$ and $x = \infty$) and shows only slight variation over this range. The rapid variation of H observed for $x_n^0 = 8$ as ϕ approaches unity also appears when $x_n^0 = 20$, but the minimum in H has now become deeper.

Figure 1 shows the variation with ϕ of the reduced, dimensionless coefficient of $(s_x - s_1)$ that we designate as H, which is defined as follows:

$$H \equiv \Delta s/(s_x - s_1) = (v_1^1 v_2^1)[1 - 1/x - (y-1) \times (v_{2a}^1/x_{na}^1 v_2^1) - [(x_{nr} - 1)v_{2r}^1/x_{nr}v_2^1]/(v_2^1 + v_1^1/x)] \quad (37)$$

Here, H has been evaluated at $x = x_n^0 = 8$ and $x = \infty$ over the range of ϕ. The most striking feature in this figure is the rapid variation of H with ϕ as ϕ approaches unity. Also, although increasing x from its most probable value of $x = 8$ to $x = \infty$ causes the value of H to increase, it does not do so significantly. That is to say, the extent to which the surface tension is lowered, for positive values of $(s_x - s_1)$, relative to that of the isotropic phase is nearly the same for $x = x_n^0$ as for $x = \infty$.

The variation of H for large ϕ at $x = x_n^0 = 8$ is more readily observed in Figure 2, where the log of $(1-\phi)$ is plotted against H. As we have shown,[3] in the limit where ϕ goes to unity, i.e., when the solute in the isotropic phase retains the most probable distribution, any solute that precipitates as an incipient anisotropic phase will be undiluted, i.e., $v_2 = 1$. Therefore, because $v_1 = 1 - v_2 = 0$, H vanishes in the same limit. A little thought leads to the conclusion that the approach of H to 0 in the limit where ϕ goes to 1 will be infinitely protracted. Physically, this behavior represents the lowering of surface tension that arises from self-ordering in the monolayer as a purely isotropic liquid is diluted with relatively small amounts of an anisotropic phase. Again note that the slope of H changes sign around $1 - \phi \approx 0.01$. The convergence of the isotropic and anisotropic solute volume fractions to unity at $\phi \approx 0.224$ has the consequence of causing H to vanish because at that point $v_1 = 1 - v_2 = 0$.

It is worth examining the behavior of H at $x = x_n^0 = 8$ as ϕ approaches 0.224 in more detail, however. In Figure 3, H has been plotted against ϕ on a greatly expanded ordinate. We immediately note that near $\phi \approx 0.34$, H takes on positive values, before achieving a maximum value around $\phi \approx 0.28$ and falling to zero at $\phi \approx 0.224$. Physically, the significance of H becoming positive is that the magnitude of the surface tension in the anisotropic phase is then higher than that of the isotropic phase {for positive values of $(s_x - s_1)$}. On the scale represented in this figure, there is no detectable difference between H evaluated at $x = \infty$ and at $x = x_n^0$.

The parameter H as a function of ϕ for $x = x_n^0 = 20$ at $x = x_n^0$ and at $x = \infty$ appears in Figure 4. Note that

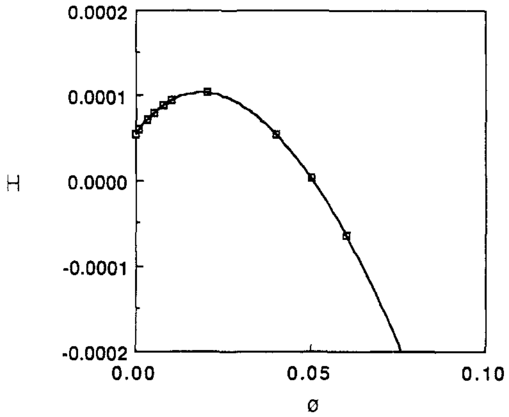

Figure 5. In the region of ϕ approaching 0 for the case of $x_n^0 = 20$, H becomes positive between roughly $0 \leq \phi \leq 0.05$. In this interval, the isotropic phase may have a lower surface tension than the anisotropic monolayer.

increasing x_n^0 from 8 to 20 causes H to increase in magnitude (see Figure 1). Qualitatively, Figure 4 reproduces much of the behavior already observed in the case of $x_n^0 = 8$ (see Figure 1), in particular, the rapid variation of H with ϕ as ϕ approaches unity. It is significant, however, that the minimum in H falls appreciably (from $H \approx -0.02$ at $x = x_n^0 = 8$ to $H \approx -0.18$ at $x = x_n^0 = 20$ for $\phi \approx 0.99$) as x_n^0 is increased. This relatively large decrease in H, which ultimately is a consequence of the greater fractionation efficiency for species of higher average length,[3] suggests that the effects predicted by this theory should be particularly evident in highly isotropic biphasic solutions having large values of x_n^0.

In the limit that ϕ goes to 1.0 (i.e., in the presence of a purely isotropic phase), v_2 goes to unity, and H vanishes for the same reason already considered for the case of $x_n^0 = 8$. Figure 5 shows the other end of the scale, where the anisotropic phase retains the most probable distribution ($\phi = 0$). As ϕ approaches this limit, H increases, first becoming positive near $\phi \approx 0.05$ and then achieving a maximum value around $\phi \approx 0.02$ before decreasing to $H = 5.5 \times 10^{-5}$ at $\phi = 0$. As before, positive values of H signify that the surface tension of the anisotropic phase is higher in this range than is that of the isotropic phase, for positive values of $(s_x - s_1)$. It is also worth pointing out that, on the scale of this figure, there is no detectable difference between H evaluated at $x = \infty$ and H at $x = x_n^0$.

The general case of $\phi = 0$, corresponding to a completely anisotropic solution, also deserves special attention. As seen from Figure 6, in which $x_n^0 = (1 - p)^{-1}$ has been plotted as a function of H from the lower limit at $x_n^0 = 17.76$ ($v_1 = 1 - v_2 = 0$; $H = 0$) out to $x_n^0 = 50$, it is only when x_n^0 is greater than or equal to about 42 that H becomes negative. The physical significance of this result is that for positive values of $(s_x - s_1)$ the incipient isotropic phase that separates out of the parent anisotropic phase will have a lower surface tension than the parent phase for $17.76 < x_n^0 < 42$. At larger values of x_n^0, the anisotropic phase will have the lower surface tension.

As noted previously,[3] the range of x_n^0 over which undiluted solute coexists in the isotropic and anisotropic phases is broad, extending approximately from $x_n^0 = 2.31$ at $\phi = 1$ to $x_n^0 = 17.76$ at $\phi = 0$. Because $v_1 = 1 - v_2 = 0$ in the absence of dilution, H must vanish over the same interval. Physically, the model predicts that the complete conversion[3] in the presence of a catalyst of an isotropic phase (in which relatively short rods are randomly distributed) to an anisotropic phase (of very long rods) will be unaccompanied by a change in surface tension.

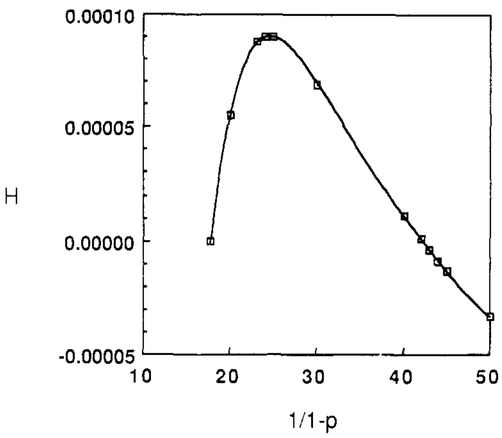

Figure 6. In the limit that the mixture consists entirely of an anisotropic phase in which the rodlike particles have a most probable distribution of axial ratios, the number average molecular chain length is $x_n^0 = (1 - p)^{-1}$. As this figure indicates, there exists a range of average axial ratios ($x_n^0 \sim 17.76$–42) for which an incipient isotropic phase has a surface tension lower than that of an anisotropic monolayer. At larger values of x_n^0, however, the surface tension of the ordered monolayer assumes the lower value.

Conclusion

Self-ordering at surfaces provides a unique path for the lowering of surface tension in rigid-rod solutions. Using the rigid-rod approximation developed by Flory,[1] we have formulated an expression for the surface tension of an anisotropic monolayer separating out of a two-phase solution of ordered and disordered rods. However, because naturally occurring systems rarely involve monodisperse distributions of species, we extended our treatment to include polydisperse mixtures[2] and, in particular, to include solutions for which axial ratios can be represented by the most probable distribution.[3]

The separation of an anisotropic monolayer out of a two-phase solution in which the parent phase has a most probable distribution of axial ratios has been shown earlier to be a consequence of particle asymmetry.[3] In solutions of rodlike particles where the volume ratio of the isotropic phase to the anisotropic phase is sufficiently large, theory predicts self-ordering to be a remarkably efficient mechanism for lowering surface tension.

In the limit where the parent phase is completely disordered, the spontaneous precipitation of an anisotropic monolayer is incapable of lowering the surface tension. However, once the isotropic phase has been diluted by even a minuscule amount of incipient anisotropic phase, self-ordering at a surface results in a lowering of surface tension.

Acknowledgment. I am indebted to Drs. A. Hindmarsh, M. Durst, S. Verrill, F. Fritsch, D. Balaban, and T. Suyehiro for helpful discussions and to Ms. M. A. Esser for reading the manuscript.

References and Notes

(1) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(2) Flory, P. J.; Abe, A. *Macromolecules* **1978**, *11*, 1119.
(3) Flory, P. J.; Frost, R. S. *Macromolecules* **1978**, *11*, 1126.
(4) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660.
(5) Prigogine, I.; Marechal, J. *J. Colloid Sci.* **1952**, *7*, 122.
(6) Prigogine, I. *J. Chim. Phys.* **1950**, *47*, 33.
(7) Because the concern of this paper is with phase incipience at a surface in contact with and in chemical equilibrium with a bulk liquid, it follows that the value of y in the monolayer should be the same as in the bulk. Clearly ordering in an isolated monolayer is a different problem—one that would require reformulation of the disorder parameter to take into account additional orientational constraints.