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Surface Tension of Mixtures of Rodlike Particles: Monomer Effects

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Received June 23, 1988; Revised Manuscript Received September 12, 1988

The surface tension of an anisotropic monolayer was recently evaluated for athermal mixtures in which the solute comprises rodlike molecules having the familiar Flory distribution of axial ratios.[1] Reconsideration of the calculations in ref 1 has shown that the manner in which the surface tension function

$$H(x) = \left[\frac{v_1{}^{l}v_2{}^{l}}{v_2{}^{l} + v_1{}^{l}/x}\right]\{1 - 1/x - (y - 1) \times (v_{2a}{}^{l}/x_{na}{}^{l}v_2{}^{l}) - (x_{nr}{}^{l} - 1)(v_{2r}{}^{l}/x_{nr}{}^{l}v_2{}^{l})\}$$

was previously evaluated overweighted the contribution from monomer present in the anisotropic phase. Correction for this problem suggests that the disordered monomer in the anisotropic phase may play a significant role in lowering surface tension. Here, as before, v_1 and v_2 are the volume fractions of solvent and solute in the liquid (superscript l), y is a disorder parameter whose generality is believed to exceed the limitations of the lattice model, and v_{2r}, v_{2a}, x_{nr}, and x_{na} represent the solute volume fractions and number average; axial ratios, x, correspond to randomly oriented (subscript r) and ordered (subscript a) solute species in the anisotropic phase, respectively. As previously defined,[1] when H is positive, the isotropic phase has a lower surface tension than the anisotropic phase, and when H is negative, the anisotropic phase has the lower surface tension.

Consider Figure 1, where H has been reevaluated as a function of the relative volume of isotropic phase ϕ for two values of x, $x = 1$ and $x = x_n{}^0 = 8$. Although there is still the rapid variation in H in the vicinity of $\phi = 0.99$, noted previously for the case $x = x_n{}^0 = 8$, two important effects can now be seen that did not show up before. The first is that H is positive for this value of x over the entire range of ϕ for which biphasic equilibria exists; the second is that H is 1 order of magnitude larger than previously calculated. The significance is that, for this value of x, the surface tension of the anisotropic phase will never be lower than that of the coexisting isotropic phase. Other observations, i.e., that H vanishes at the limits $\phi \approx 0.224$ and $\phi = 1.0$ and that the effect of increasing x from 8 to infinity on the behavior and magnitude of H is relatively small, continue to be valid.

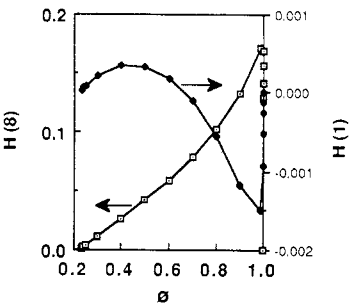

Figure 1. Surface tension function $H(x)$ representing self-ordering effects in an anisotropic monolayer that is in equilibrium with a biphasic solution of rigid rods for a most probable (Flory) distribution of axial ratios having $x_n{}^0 = 8$. The function has been evaluated at two axial ratios, $x = 1$ and $x = 8$. Note: When $H < 0$, the anisotropic phase has the lower surface tension, and when $H > 0$, the surface tension of the isotropic phase is lower. Although not apparent in the figure, H actually vanishes at four values of ϕ for $x = 1$ (see text).

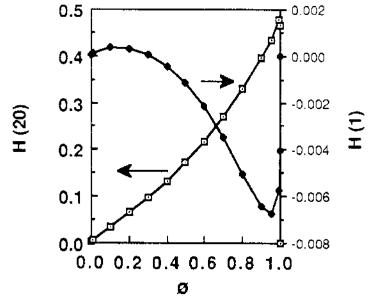

Figure 2. Surface tension function $H(x)$ for self-ordering for $x_n{}^0 = 20$ evaluated at $x = 1$ and at $x = 20$. Unlike the case of $x_n{}^0 = 8$, one can have biphasic equilibria for the mixture of rods for this value of $x_n{}^0$ when $\phi = 0$. The parameter H is small but greater than zero in this limit. Analysis shows that there are three values of ϕ for which H vanishes when $x = 1$, only two of which can be seen in the figure.

We next consider H as a function of ϕ for $x = 1$, corresponding to a disordered monomer component within the anisotropic phase.[2] From Figure 1 it is seen that although the absolute magnitude of H is small, the function changes sign at $\phi \approx 0.7$. The change in sign of H turns out to be a consequence of y crossing the $y = 1$ boundary. Analysis shows that the function remains negative for larger values of ϕ until $1 - \phi = 2.1 \times 10^{-8}$, where again $y = 1$ (see ref 2, p 1131). For larger values of ϕ, H is again positive. In the limit that $\phi = 1.0$, $H = 0$ as already noted. The fact that H is positive for ϕ very close to 1.0 means that the presence of monomer in the anisotropic surface layer cannot bring about a lowering of surface tension in this region. However, over the range of ϕ indicated, the disordered component ($x = 1$) of the anisotropic phase will have a lower surface tension than the bulk isotropic phase.

In Figure 2, H has been similarly recalculated as a function of ϕ for $x_n{}^0 = 20$, evaluated at $x = 1$ and at $x = x_n{}^0 = 20$. Although there is little qualitative difference seen in the behavior of H vs ϕ in Figures 1 and 2, there are two features of note: the range of H is now larger, and H now assumes negative values for $x = 1$ for ϕ as small as ~0.3. The surface tension of the monomer in the anisotropic phase is thus seen to be a stronger function of ϕ for the case $x_n{}^0 = 20$ than for $x_n{}^0 = 8$.

The behavior predicted for the case $\phi = 0$, corresponding to a completely anisotropic solution, also changes in light of the new calculations. Specifically, H is greater than or equal to zero for all species x. According to theory, the incipient isotropic phase will always have a surface tension that is lower or equal to that of the parent anisotropic phase.

References and Notes

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