Thermodynamics of Phase Separation in Mixtures of Associating Polymers and Homopolymers in Solution

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ABSTRACT: The phase behavior of mixtures of a hydrophobically modified polymer capable of forming associations and an unmodified polymer of the same chemical composition has been investigated. The associative thickener (AT) consists of poly(ethylene glycol) (PEG) end-capped at both ends with hydrophobic alkane groups. It is found that mixtures of the AT solution and the unmodified PEG phase separate into two distinct solutions, provided AT molar fractions are <0.65. This is despite the fact that the overall polymer concentration throughout both phases remains the same. However, the viscosities of the two phases were found to be very different. For example, for a 50:50 mixture at an overall concentration of 5 wt %, the viscosity of one phase was found to be 170 Pa s, consistent with the existence of an AT network, whereas the viscosity of the less viscous solution was measured to be 0.004 Pa s, indicating that nearly all the polymer in this phase is of the unmodified type. When the AT to total polymer ratio is >0.65 or when the overall polymer concentration is below 2%, no phase separation is observed. It is proposed that the phase separation behavior in this type of system is an entropically driven phenomenon. It is shown that by considering the entropy changes due to the association of the end groups, within a Flory–Huggins framework, all of the above features can be accounted for theoretically.

Introduction

In recent years there has been a growing interest in the phase behavior of polymers in solution. Traditionally, the phase behavior of a single polymer in solution is treated using the well-known statistical theory developed by Flory[1] and Huggins.[2] Despite its shortcomings, this has provided a good qualitative description of the phase behavior of such systems. Several attempts have been made to provide more thorough statistical models such as those by Widom[3] and Aguilera-Granja and Kikuchi.[4] The possibility of association between polymers in solution has interesting consequences on their phase behavior. For example, in aqueous polymer solutions, the possibility of hydrogen-bonding and other more complex interactions than the usual two-body interaction between monomers can arise. Attempts have been made to theoretically include such effects in the Flory–Huggins scheme. For example, Yu et al.[5] have described the reversible associations occurring between a polymer and solvent as would arise through H-bonding in, for example, poly(ethylene oxide) (PEO) solutions. To do this the polymer and its associated H-bonded solvent molecules are treated as a separate species in its own right. In an alternative treatment, de Gennes[6] has invoked the existence of more complicated interactions than usual two-body ones. In particular, he has proposed a case in which three or more monomers can form a loose cluster arising from the existence of higher-order attractive interactions. Other examples of self-associating polymer systems which have been studied theoretically include ionomers[7] and polymeric micelles.[8] It is clear from these studies that the effect of intermolecular association is to give rise to an effective attractive interaction. This has been supported by simulation studies of associating polymers by Groot and Agterhof[9] and Baljon-Haakman and Witten[10] and by experimental studies demonstrating phase separation in polymer gels in close proximity to the Θ-temperature.[11]

As well as the single-polymer case, there has been a growing interest in the phase behavior of mixtures of two polymers in aqueous solution. In the main, research interest has concentrated on the experimental studies of such systems and has included studies of mixtures of nonionics and ionics and their various combinations. This area has been reviewed recently by Piculell and Lindmann.[12] It is apparent that, for almost all cases of current interest, the chemical incompatibility between the two polymers is the driving force for any phase separation behavior.

In this paper we shall consider the phase behavior of a system that is somewhat different from the cases mentioned above. In particular, we consider mixtures of an associating hydrophobically modified water-soluble polymer with a nonassociating unmodified polymer of the same chemical composition. The associating polymers used are the so-called HEUR (hydrophobic ethoxylated urethane) associative thickeners (AT) comprising poly(ethylene glycol) (PEG) chain extended by short diisocyanates and end-capped by hydrophobic alcohols. These polymers can, in essence, be considered to be amphipathic telechelic polymers of the ABA type where the B block is a long hydrophilic section and the A blocks are very short hydrophobes. ATs in solution have attracted widespread interest due to their ability to form micellar associations and, as a consequence of their telechelic nature, to build transient networks.[13] A schematic picture of such a network is shown in Figure 1. The homopolymer used is PEG of comparable molecular weight to the AT. It is clear that in one sense this system can be considered to be a mixture of two different polymers. However, in this case, due to the similarity between the homopolymer and the polymeric part of the AT, there will be no chemical incompatibility to drive phase separation in the traditional Flory–Huggins sense. In the absence of any chemical incompatibility between the monomers of the two polymer species, it remains that the strong tendency of the AT to form micelles must be considered to be the origin of any phase separation behavior. That is to say that the phase separation behavior of these systems is essentially an entropy-driven phenomenon, in a sense that will become clear later. The same type of considerations also arise in

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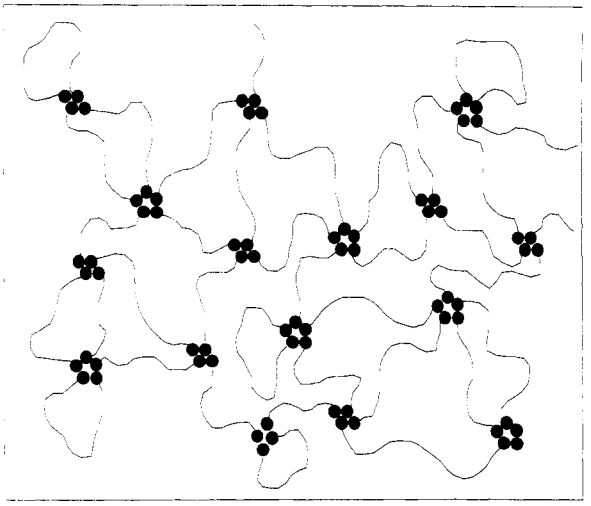

Figure 1. Schematic picture of an associative thickener network showing chains in both looped and bridged conformations.

a number of other systems. Drye and Cates[8] have studied one such system consisting of surfactants forming long tubelike micelles. These are then treated as polymer chains. These chains can break up at any point to create free ends. Under suitable conditions the free ends can fuse back to neighboring micelles to form branch points. Drye and Cates[8] have shown that the entropy change associated with the formation of such junctions plays a significant role in determining whether the surfactant remains in the solution or phase separates. Similar factors are at work in the present system studied here. Note that for certain polymers the formation of associations and the resultant gel formation can lead to the phase separation of the associating polymer from solution. This has not been observed in pure solutions of the associating polymer considered here.

That ATs can form micellar associations has been confirmed spectroscopically by several workers.[14-16] It appears that a typical aggregation number lies in the region of 6–10, although this is a matter of some debate.[15,17] We have recently published an account of the rheological properties of ATs in solution and interpreted our finding in terms of transient network theory.[13] Our work showed that ATs behave as Maxwell fluids with a single viscoelastic relaxation time. This observation was shown to be consistent with the general prediction of Tanaka and Edwards[18] in which the process governing stress relaxation is the time scale for the detachment of a hydrophobe from a micelle. Supposing that the rate of detachment, β_0, is independent of chain extension, this time scale is given by

$$\beta_0 = \omega_0 \exp\left(\frac{E_m}{kT}\right) \tag{1}$$

where E_m is the activation energy for disengagement, assumed to be equal to the binding energy of the micelle, and ω_0 is a characteristic frequency of thermal vibration of order 0.1 ns. The elastic modulus of such networks is given by the theory of Green and Tobolsky[19]

$$G_\infty = \nu kT \tag{2}$$

where ν is the number density of elastically active chains. Tanaka and Edwards showed that for $E_m \gg kT$, as is found for ATs,[13] ν was equatable with n, the number density of chains. However, Tanaka and Edwards only considered the possibility that chains could exist as transient cross-links or as elastically inactive dangling ends (i.e., they only considered a fully developed network). To describe our observations of the concentration dependence of the elastic modulus, we developed a simple statistical model describing the various possible chain states within the network. It turned out that the presence of chains in looped conformations must be invoked to explain the observed experimental trends. A looped chain is one in which both ends of the same chain reside within the same micelle and is thus elastically inactive. The concentration dependence of the rheological coefficients could then be ascribed to a transition between a network built predominantly of looped chains to one in which links prevail at high concentrations. As we shall see during this paper, the presence of looped and linked conformations also has some bearing on the phase behavior of ATs in the presence of nonassociating polymer.

Experimental Section

Materials. The associating polymer used in this work was prepared according to the synthetic procedures described by Emmons and Stevens.[20] The dried poly(ethylene glycol) is reacted with isophorone diisocyanate which acts as a coupling agent for the end-capping alcohol, in this case hexadecanol. The polymer was purified by multiple reprecipitation from warm toluene into either diethyl ether or hexane to remove free alcohol and adducts of the diisocyanate and the alcohol. This procedure does not remove un-end-capped PEG from the product, and our earlier rheological measurements suggest a significant number of chain ends without hydrophobes (of the order 10% or so). The associating polymer produces an optically clear solution at all concentrations studied and provides viscosity enhancement above a concentration of approximately 1% w/v. Gel permeation chromatography gave a molecular weight (M_w) of 33 100 and polydispersity (M_w/M_n) of 1.47. The homopolymer was poly(ethylene glycol) of molecular weight 35 000 obtained from Fluka and was used as supplied.

Solutions were prepared from stock solutions of the two polymers of the same concentration and mixing the two solutions in differing ratios. Thus the overall polymer concentration is kept at a fixed level and the ratio of the two polymers varied. The mixtures were thoroughly mixed by warming (to reduce viscosity) and vigorous shaking. All samples initially appeared homogeneous after this treatment. The samples were then left to equilibrate at 25 °C. All observations reported are at this temperature.

Rheology. Rheological measurements were performed on a Bohlin VOR rheometer. Oscillatory tests were performed over the frequency range 0.1–10 Hz and at a strain amplitude of 10%, which is well within the linear viscoelastic region for these polymers. Flow curves were determined over the shear-rate range 10–200 s^{-1}. The measuring system was either a concentric cylinder (14 mm i.d. with a 1 mm gap) or a cone and plate (5 cm/5°) depending on the viscosity of the sample.

Determination of Polymer Content. The method of Baleaux[21] was used to determine the PEG/AT content in a particular phase. The technique involves complexation of the ethylene oxide (EO) chains with I_3^-, and since both AT and PEG comprise mainly EO, this technique does not resolve the two separate polymer concentrations but rather determines the overall polymer concentration in a particular phase. A typical procedure is as follows: A solution of potassium iodide and iodine (1 g of I_2 and 2 g of KI in 100 mL of water) was added to the isolated phase to be analyzed (at the level of 1 mL of KI/I_2 to 40 mL of PEG solution). The resulting mixture was then diluted to levels such that a clear gold brown solution was obtained and the UV absorbance determined. The concentration of PEG was then obtained from a UV calibration curve constructed over the concentration range (1–5) × 10^{-3} wt %.

Results

The phase behavior of a series of polymers was examined at several overall polymer concentrations and for varying mole fractions of AT (X_A = [AT]/([AT] + [PEG])). The AT and PEG solutions were mixed in such a fashion as to keep the overall polymer concentration at a fixed value while altering the ratios of the two polymer components.

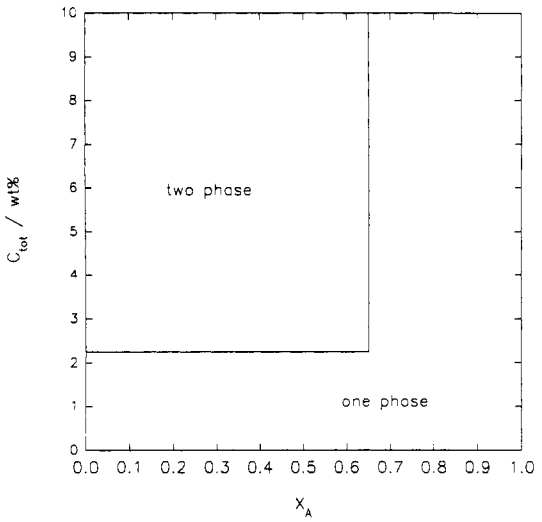

Figure 2. Experimental phase diagram for mixtures of AT and PEG (MW = 35000, T = 298 K).

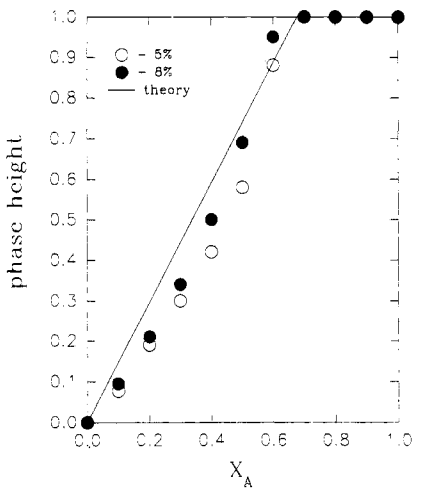

Figure 3. Comparison of experimental and predicted phase heights for the AT-rich phase as a function of molar fraction of AT.

The resultant phase diagram at a temperature of 25 °C is shown in Figure 2. As can be seen, at a total concentration below about 2 wt % the mixtures were found to be stable irrespective of composition. At higher polymer concentrations, however, a region of instability was observed for $0 < X_A < 0.65$. In this region the samples separated into two distinct layers, both of which appear optically clear. At higher fractions (>0.65), the mixture is one phase and is optically clear. Note that the errors on the horizontal and vertical phase boundary lines are respectively ±0.25 wt % and ±0.05. The estimated phase heights as a function of composition at overall polymer concentrations of 5 and 8 wt % are shown in Figure 3. As can be seen, in general, the phase height of the lower AT-rich phase (see below) is always larger than its molar fraction X_A.

Rheological measurements were performed on the two separated phases to determine the level of AT within each phase. Significant viscosity enhancement would be expected if either phase contains more than 1% w/v AT.[13] The viscosity of the two phases was recorded for each separate phase of a 50:50 mixture of AT and PEG at an overall polymer concentration of 5%. The viscosity of the lower phase was found to be 170 Pa s, whereas the viscosity of the upper phase was found to be in the region of 0.004 Pa s. This latter figure is of comparable magnitude to a pure PEG solution at about these concentrations and molecular weight, although the accuracy of the measurement is insufficient to determine the PEG content with any certainty. The very low viscosity indicates that the upper limit of AT in this phase is 1 wt %, although it may be that the concentration is considerably less than this. The vast difference in the viscosity of the two phases was typical of all of the phase-separated samples examined.

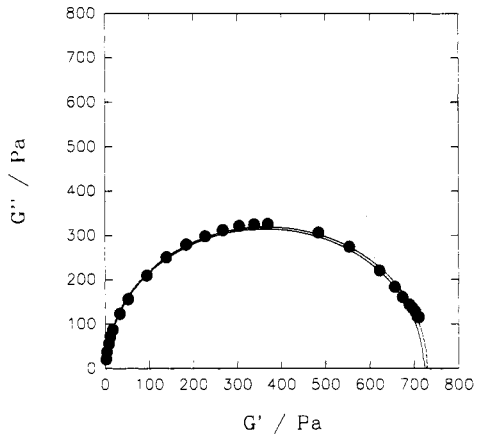

Figure 4. Cole–Cole plot of the viscoelastic moduli for the isolated lower phase of a 50:50 mixture of AT and PEG at an overall polymer concentration of 5% (MW = 35000, T = 298 K): solid line, fit to eq 3 with m = 0.5; dotted line, fit with m = 0.49.

Figure 4 shows the viscoelastic response of the lower phase of the 50:50 mixture at an overall polymer concentration of 5%. The data are shown in the form of a Cole–Cole plot of storage modulus, G', versus G''. For a fluid with a single viscoelastic relaxation time (a so-called Maxwell fluid), the data would be expected to be in the form of a semicircle and to be described by

$$G''(\omega) = (G'(\omega)G_\infty - G'(\omega)^2)^m \qquad (3)$$

where m = 0.5. As can be seen the data are in the form of a semicircle, thus confirming that the network of ATs possesses a single viscoelastic relaxation time. Allowing m to float gave a best fit when m = 0.49. This is as expected since the rheological response of the viscous phase will be dominated by the AT network, which, as discussed in the Introduction, is known to be governed by a single relaxation process. The relaxation time for this sample is approximately 0.14 s, and the elastic modulus (G_∞) is 720 Pa. The modulus of the upper phase was found to be too small to be measurable using this technique.

The overall polymer content in the two phases was determined using the spectroscopic technique described in the Experimental Section. The method determines the concentration of ethylene oxide groups within a particular phase and thus does not discriminate between associative thickener or the unmodified homopolymer. As a consequence, the technique only measures the overall polymer concentration within each phase. It was found that within the experimental error of the technique the two phases contained identical concentrations of polymer irrespective of overall concentration or composition. By combining this information and the rheological data presented above, it can be surmised that one phase is largely AT and the other largely PEG.

Discussion

Theory. To form a theoretical picture of the phase separation behavior of the mixed solutions of AT and homopolymers, let us first consider a simple case of two very similar polymer solutions. We shall assume that the polymer volume fraction in both solutions is ϕ. Furthermore, we assume that the polymer chains in both cases are

exactly the same in every respect, except that in one of the solutions they have small markers attached to their ends. These markers are much smaller than the chains themselves, so as to have no significant effect on the MW or other properties of the polymer. From now on, to distinguish the two species from each other, we shall refer to the marked chains as A and to the unmarked ones as B. According to the classical Flory–Huggins theory,[1] the free energy per site (in a lattice model) for both solutions is given by

$$\frac{F}{kT} = (1-\phi)\ln(1-\phi) + \frac{\phi}{N}\ln\phi + \chi\phi(1-\phi) \qquad (4)$$

where N is the repeat units of the polymer chain and χ the Flory parameter specifying the interaction of the monomers with the solvent molecules. From the above discussion, it is clear that N and χ have the same value for both solutions. Now, consider the free energy of mixing, that is, the resulting free energy above that of the "pure" solutions, which arises when a fraction X_A of the solution A is mixed with a fraction $X_B = (1 - X_A)$ of the solution B. Once again, this free energy can readily be calculated within the framework of Flory–Huggins theory. Per lattice site this is given by

$$\frac{F_{mix}}{kT} = \frac{\phi}{N}[X_A \ln X_A + (1-X_A)\ln(1-X_A)] \qquad (5)$$

Note that since all the monomers involved are the same, no Flory interaction term χ_{AB} appears in (5). $F_{mix}(X_A)$ is a convex function of X_A everywhere. It follows that for all compositions the two solutions mix and that there is no phase separation. This is of course expected as in every respect the two groups of polymers are identical, only distinguishable by the virtue of the small markers on the group A polymers.

So far, the markers only serve to identify the two groups of polymers. The above picture is considerably altered if now the markers consist of hydrophobic end groups with a strong tendency for micellization. When the micellization energy $E_m \gg kT$, which is the case for the AT solutions studied here,[13] an overwhelming number of the end groups happen to be within micelles at any one time.[13,18] That is to say that, out of all the possible configurations available to an end-capped chain, only those in which the chain starts and terminates within a micelle have any significant chance of occurrence. This at once implies a severe reduction in the number of degrees of freedom available to the system, and hence a drop in the entropy. In the case of free polymers, chains can start and end at points independent (or almost independent, if excluded volumes effects are considered) of each other. For end-capped chains, once the starting position of one chain is specified, on average a further $(N_{aggr} - 1)$ polymers are constrained to begin or terminate at the point. N_{aggr} is the mean aggregation number for the hydrophobic end groups in one micelle, with a typical value of 6 for our AT system.

The above restrictions can be built into the Flory–Huggins lattice model along the same lines as those outlined by Drye and Cates[8] in their study of pure "AT-like" solutions. One notes that, if the total number of lattice cells is V, then a total of $X_A\phi V$ sites are occupied by monomers of the end-capped polymer chains and $X_B\phi V$ by those of the non-end-capped polymer chains. Thus, one has $X_A\phi V/N$ end-capped polymers, each of which contributes two hydrophobic end groups to the formation of micelles. The total number of micelles in the system is then

$$n_m = \frac{2}{N_{aggr}}\left(\frac{X_A\phi V}{N}\right) \qquad (6)$$

We start by specifying the positions of these n_m micelles on the lattice. This can be accomplished in $V!/((V - n_m)!n_m!)$ possible ways. Note that by doing this we have already made an implicit assumption regarding the micelle–micelle radial distribution function by setting $g(r) = 1$. At present, there is no clear evidence supporting or disproving this matter. Although it is quite likely that on length scales comparable to the radius of gyration of the chains $g(r)$ has a more complicated structure. For more macroscopic length scales the assumption seems reasonable. This is demonstrated by the optical clarity of the prepared AT solutions. In any case, we believe that small deviations from $g(r) = 1$ only serve to complicate the calculations, without qualitatively changing the picture presented in here.

With the position of micelles determined, next the end-capped chains are introduced one by one onto the lattice. Each such polymer has a choice of n_m sites (micelles) from which it can begin its "random walk". This gives a total number of

$$\frac{n_m^{(X_A\phi V/N)}}{(X_A\phi V/N)!}$$

ways for starting the chains. As usual, the term $(X_A\phi V/N)!$ in the denominator reflects the fact that the end-capped chains are indistinguishable from each other. The "random walk" for each polymer proceeds in the same manner as outlined in the original Flory–Huggins model,[1] with one exception. All the configurations that do not end on a micelle are not acceptable. Since micelles are randomly distributed, any site has a probability of $n_m/V = (2X_A\phi)/(N_{aggr}N)$ of being occupied by a micelle. That is to say that out of all possible configurations available to a chain starting on a micelle, on average only a fraction $(2X_A\phi)/(N_{aggr}N)$ also result in the termination of the chain on a micelle. It is clear that this introduces a further factor

$$\left(\frac{2X_A\phi}{N_{aggr}N}\right)^{(X_A\phi V/N)} \qquad (7)$$

into the calculations. Note that we include all the possible states, irrespective of whether they give rise to a full network or finite clusters of polymer chains. Which one of these will dominate is an interesting problem that goes beyond the scope of the present paper but has been considered by Tanaka[22] in a somewhat different context.

Once again, in writing (7), a certain assumption regarding the loops (chains that have both their end groups in the same micelle) had to be made. All configurations in which the end hydrophobe returns to the original micelle are guaranteed to be successful. For these there is no need to introduce the factor $(2X_A\phi)/(N_{aggr}N)$. At high polymer concentrations there are many micelles within a distance R_G of a given micelle. R_G here is the radius of gyration of the chains. As such, a polymer chain has many more states leading to the formation of a link, that is, having its two ends in different micelles. The wrong factor for the loop states is therefore not of great significance for the calculations. As the polymer concentration is decreased, however, there comes a time when the intermicellar separations become much larger than R_G. Now the number of loop configurations becomes dominant. In this case the approximation inherent in (7) is no longer valid.

For the time being we shall assume that our approximation is acceptable at all concentrations by considering the limit of long chains $N \rightarrow \infty$. We shall return to the problem of finite N later.

Once the end-capped A chains are all in place, the B chains, followed by the solvent molecules, are introduced into the lattice. The procedure for this is precisely the same as that in the usual Flory–Huggins treatment. Taking into account all the terms discussed above, it is possible to derive an expression for the entropy and hence the free energy of the system. As usual, when the free energy is measured in reference to the free energy of the two unmixed components, the linear and constant terms in X_A drop off.[23] Ignoring terms of the order $(n_m/V)^2$ or higher (the volume fraction of micelles is indeed very small), one arrives at the following expression for the free energy per site:

$$\frac{F_{mix}}{kT} = \frac{\phi}{N}\left\{\frac{2}{N_{aggr}} X_A \ln(X_A) + (1 - X_A)\ln(1 - X_A) - X_A \ln(X_A)\right\} \quad (8)$$

Note that in the special case where the end groups on the A chains do not form micelles one has $N_{aggr} = 1$. Substituting this value into (8), we obtain the expected result (5). Also for the case $N_{aggr} = 2$, provided one can still ignore the loops, all the AT polymers join to make a very long single chain. Within the limitations of the Flory–Huggins theory, the free energy contribution from this long chain will be zero, leaving $F_{mix}/kT = (\phi/N)(1 - \phi_A)\ln(1 - \phi_A)$ as the sole remaining term. Once again, we see that eq 8 reproduces this result when $N_{aggr} = 2$. It is interesting that the first and the last terms in eq 8 also appear in the free energy expression derived by Drye and Cates[8] for certain surfactant solutions forming tubelike micelles. This indicates the importance of the entropy term associated with the formation of junctions in these systems.

Before we consider the implications of eq 8 for the phase separation behavior of the system, it is worthwhile briefly discussing the origin of each of the terms in it. Starting with the middle term $(1 - X_A)\ln(1 - X_A)$, this is the same as that appearing in eq 5. This term is associated with the non-end-capped B polymer, which, of course, remains the same as before. Of more interest is the first term, which has changed from $X_A \ln(X_A)$ to $(2/N_{aggr})X_A \ln(X_A)$. When the chains are free to begin their walk from any point on the lattice independent of each other, one has $(X_A\phi/N)$ degrees of freedom associated with this. However, the end-capped polymers are only free to start from $(2X_A\phi/N_{aggr}N)$ micelles. Thus there is a drop in the number of degrees of freedom by a factor $(2/N_{aggr})$, which now multiplies the term $X_A \ln(X_A)$ in (8). Finally, the last term is $-X_A \ln(X_A)$. It is this term that drives the phase separation in the mixture. We believe that it arises due to the following reason. Consider a single chain starting from a given micelle. If the concentration of the end-capped polymer in the neighborhood of this chain is doubled, then the number of nearby micelles would also double. Assuming a uniform distribution of micelles, this means that there are now twice as many points on which the chain can end. That is a factor of 2 increase in the number of configurations available to the chain, giving rise to an increase of ln(2) in the entropy. Thus, there is an entropy term favoring the end-capped chains to cluster together. From this discussion, it is clear that there is a contribution of the form $\ln(X_A)$ in the entropy for each chain, giving rise to the term $-X_A \ln(X_A)$ in the free energy of mixing. The existence of an effective attractive interaction as a result of association, has already been highlighted by the calculations of Cates and Witten,[24] Drye and Cates[8], and the simulation work of Baljon-Haakman and Witten[10] among others.

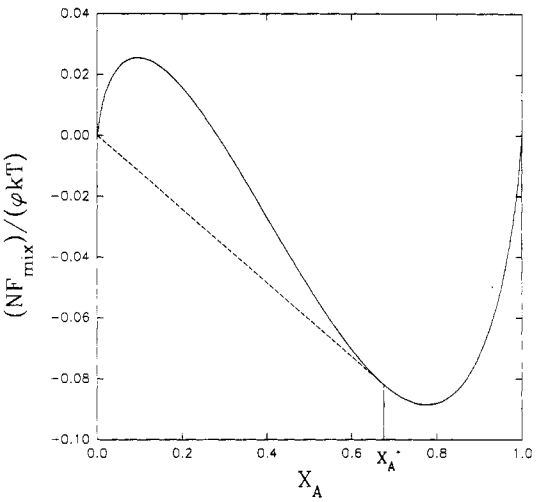

Figure 5. Free energy of mixing in the limit $N \rightarrow \infty$ when a solution of end-capped PEG polymer (AT) is mixed with that of an unmodified one. When the AT to total polymer concentration is less than X_A^+, the system phase separates into two distinct solutions. Above that, we have a single phase.

Figure 5 shows $(NF_{mix}/\phi kT)$, as given by (8), plotted against X_A for a value $N_{aggr} = 6$. It is seen that when the fraction of the AT solution in the mixture is less than a limiting value, denoted by X_A^+ in Figure 5, the mixture phase separates into two solutions. One of these is rich in AT having a fraction X_A^+ of end-capped polymers and $X_B^+ = (1 - X_A^+)$ of non-end-capped polymers. The other phase is devoid of any AT chains, consisting only of homopolymers (for finite N the concentration of AT is not absolutely zero, but it is very small). Following de Gennes,[6] the value of X_A^+ can be calculated by constructing the tangent to $F_{mix}(X_A)$ such that it passes through the origin. This is schematically shown in Figure 5. The value of X_A^+ then satisfies the equation

$$\frac{F_{mix}(X_A^+)}{X_A^+} = F'_{mix}(X_A^+) \quad (9)$$

which, using eq 8, leads to

$$\frac{\ln(1 - X_A^+)}{X_A^+} = \left(\frac{2}{N_{aggr}} - 2\right) \quad (10)$$

For $N_{aggr} = 6$, eq 10 gives a value $X_A^+ = 0.68$. As N_{aggr} is made smaller, the value of X_A^+ decreases. For $N_{aggr} \gg 1$ the value of X_A^+ approaches a limiting value of 0.78.

When the concentration of the end-capped chains $X_A\phi$ is decreased, for any polymer with a finite number of repeat units N, eventually the loop configurations dominate. When this happens, eq 8 has to be modified to correctly reflect the presence of such loops. To gain some insight into the effect of these, consider a dilute system which is still above the cmc of hydrophobic end groups, which is quite small. The intermicellar distances are now much larger than the typical radius of gyration R_G for the chains, which means that most of the chains will adopt a loop configuration. There is considerable evidence, both from spectroscopic work[25] and from the rheological data,[13,17] to support this view. Now if the value of X_A is slightly increased such that the intermicellar distances are still larger than R_G, then there is also a corresponding increase

in the number of link states available to the end-capped chains. These, however, are rather insignificant compared to the number of loop configurations, which, of course, remains the same. It is clear that, in this regime, the dependence of the total number of available states on X_A is much weaker than the linear relationship suggested previously.

To partially address the above complication, consider a chain starting at a particular micelle. Without loss of generality, we shall take the position of this micelle to be the origin. Now let us assume that the possible number of ways that the hydrophobic group at the other end of the chain will also reside in the same micelle is Ω_0. The exact value of Ω_0 will depend on many parameters such as the size of the chains N and the volume of the micelles, but fortunately this is not relevant for our calculations. Now if there is another micelle at a position $\mathbf{r}$, a link between the two micelles can be formed in

$$\Omega_0 \exp\left(-\frac{3r^2}{2Na_0^2}\right)$$

possible ways, at least at concentration $\phi \geq \phi^*$. We shall take a_0 to be of the order of a monomer size, although it is more correct to identify this with the correlation length when $\phi \sim \phi^*$. Using the above expression, the total number of configurations available to the chain is

$$\Omega_{tot} = \Omega_0 \int_0^\infty [n_m g(r) + \delta(\mathbf{r})] \exp\left(\frac{-3r^2}{2Na_0^2}\right)(4\pi r^2)\, dr \quad (11)$$

where $\delta(\mathbf{r})$ is the Dirac δ function. To make progress, once again we assume that the micelle–micelle radial distribution function $g(r) = 1$, as we have done throughout the paper. Taking the volume of a single monomer to be a_0^3 and using (6), eq 11 simplifies to

$$\Omega_{tot} = \Omega_0\left(1 + \frac{4\pi^{3/2} n_m N^{3/2} a_0^3}{3\sqrt{6}}\right) = \Omega_0\left(1 + \alpha\frac{X_A\phi}{\phi^*}\right) \quad (12)$$

In deriving (12) we have also used the fact that for ideal chains $\phi^* \sim 1/N^{1/2}$. The constant α in the above equation is close to unity. As a result of eq 12, the last term in the free energy expression (8) is now modified, resulting in

$$\frac{F_{mix}}{kT} = \frac{\phi}{N}\left\{\frac{2}{N_{aggr}} X_A \ln(X_A) + (1 - X_A)\ln(1 - X_A) - X_A \ln\left(\frac{1 + (X_A\phi/\phi^*)}{1 + (\phi/\phi^*)}\right)\right\} \quad (13)$$

Note that for polymer concentrations $\phi \gg \phi^*$ and X_A not too small, eq 13 reduces to the previous result (8). This is expected since in this region the link configurations are far more probable than the loops. On the other hand, when $\phi \ll \phi^*$ the last term in (13) almost vanishes, reflecting the dominance of the loop states. As discussed above, the number of loop configurations does not depend on the number of neighboring micelles and hence is not a strong function of $X_A\phi$.

Figure 6 shows a comparison of the free energy of mixing for three different values of $\phi/\phi^* = 1$, 4, and 10. It is seen that for the case $\phi/\phi^* = 1$ the unstable region has all but disappeared. Thus, at these lower polymer concentrations the two solutions are expected to mix, at any given ratio, without becoming phase separated.

All of the above calculations were performed within the usual Flory–Huggins framework. It is no doubt possible to extend the theory beyond this approximation, as has been done in other related problems.[8] The Flory–Huggins approximation is known not to be particularly accurate for mixtures involving a polymer and a solvent phase. However, we are concerned here with the mixing of two polymer solutions, both of which are perfectly stable. Any inaccuracies in the description of the mixed phase introduced through the use of the Flory–Huggins approximation also exist in the description of the two "pure" solutions. Thus, we believe that, to a first approximation, when the free energy of mixing is calculated, such inaccuracies will tend to cancel out. In the next section we will discuss our experimental results in the light of the theory presented above.

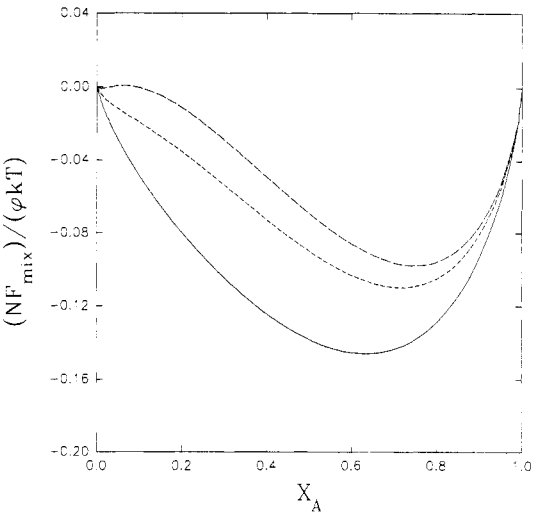

Figure 6. Free energy of mixing for solutions of AT and unmodified PEG at various values of ϕ/ϕ^*, showing the effect of loop formation at lower concentrations. The value of ϕ/ϕ^* is 10, 4, and 1 for the long-dashed, short-dashed, and the solid curves, respectively.

Comparison of Theory and Experiment

The theoretical development described above gives the following predictions for the phase equilibria for mixtures of associating polymer with homopolymer: (a) a transition between an unstable region at $X_A < 0.68$ and a stable mixing region above this; (b) A lower boundary concentration below which stability is observed irrespective of composition. As can be seen from Figure 2 these predictions agree very well with the observed phase diagrams for mixtures of AT and PEG. Such excellent agreement (cf. the predicted value for $X_A^+ = 0.68$ and the experimental result $X_A^+ = 0.65 \pm 0.05$) lends support to the "idealized" nature of this system and, in the absence of any chemical incompatibility, to the entropic origins of its phase behavior.

The composition of the two phases in the unstable region is predicted from theory to consist of identical overall monomer concentration (remembering that for this system the monomer is the same for both associating polymer and homopolymer) with one phase almost exclusively comprising homopolymer. The second phase is anticipated to consist of a mixture of homopolymer (32%) and associating polymer (68%). The rheological and analytical data shown above can be used to provide some insight into the compositions of the two phases within the phase-separated regime. First, the spectroscopic analysis shows the absence of any overall polymer concentration fluctuations irrespective of composition. Thus the monomer composition appears to be (within experimental error) the same within each phase. The large viscosity difference between the two phases provides clear evidence that one phase is predominantly associating polymer and the other largely PEG homopolymer. The upper limit of AT in the

low-viscosity phase is approximately 1 wt % (above this concentration the viscosity would be enhanced by AT network formation which would be readily detectable[13]). Thus, for example, for a 5% solution of AT and PEG at $X_A = 0.5$, the rheological data suggest that no more than 20% of the polymer resident within this phase is of the associating type. Similarly, for an 8% solution at the same composition, the upper limit is in the region of 12.5%. Thus it appears that the major component of this phase must be homopolymer. It should be stressed that these figures only represent upper limits; the actual AT content of this phase may be much lower than this. It would, of course, be highly desirable to construct an experiment to accurately determine the AT content in both phases, but at this stage, it is not clear how this can be achieved. (One possibility might involve the use of neutron scattering with deuterated homopolymer but normal AT.) As stated above, the calculations indicate that the concentration of AT chains within this low-viscosity phase would be minimal.

The viscoelastic data (Figure 4) obtained from the isolated high-viscosity phase of a 5% solution at a composition $X_A = 0.5$ demonstrate the elastic nature of this phase. The single relaxation time and the consequent semicircular Cole–Cole plot are as found for a pure AT solution. The high frequency limiting modulus for this phase was found to be 714 Pa. This value compares with that obtained for a pure AT solution at a concentration of ca. 3.5%,[13] indicating that 70% of the polymer chains are AT (assuming that the PEG has a minimal effect on the modulus of the AT network). These observations are in excellent agreement with the expectations of the statistical theory described in the preceding section.

The phase heights obtained for both 5 and 8% solutions are shown in Figure 3 along with the predictions from theory for infinite chains. As can be seen, although the agreement is not perfect, the experimental observations are broadly in line with predictions allowing for the fact that the theory has a number of implicit assumptions. It is worth noting the slow kinetics of such systems. Phase separation is visible within 24 h for most solutions, but due to the high viscosity of the AT-rich phase (particularly at high overall concentrations) and the small differences in the densities of the two phases, phase heights are not constant for several weeks. For this reason, it is difficult to be certain that the separation is complete and that the phase heights are absolutely accurate.

Conclusions

The phase behavior of mixtures of associative thickener and poly(ethylene glycol) has been investigated in solution. This system represents an ideal case since both polymers are identical except for the small hydrophobic end-capping associating groups, allowing for the realization of a system with minimal chemical incompatibility. Their phase behavior was characterized by the following features: (a) The two polymers were found to be miscible at all compositions at polymer concentrations less than approximately 2 wt %. (b) At higher concentrations the system phase separated into two phases at AT molar fractions lower than 0.65. (c) Even in this phase-separated region, the total polymer concentration was found to be uniform throughout the sample. (d) The two phases were of disparate viscosities, indicating that one phase was dominated by AT while the other was largely PEG.

In the theoretical treatment of these polymers it is assumed from the outset that there is no chemical contribution arising from contact dissimilarity between the monomers to the free energy of mixing of these two polymers. This seems justified since both polymers have the same monomer composition in the main chain, with the end groups contributing only ca. 2% of the molecules in the case of the AT chains. Furthermore, the micellization energy of the end caps is many times kT. As such, nearly all the end-group hydrophobes will be in the micelles. Thus the phase behavior can be treated on purely entropic grounds. Once the entropic effects of the association of the end-capped polymers are taken into account, it is found that the above experimental observations can be accounted for by theory.

It is clear through examination of eq 10 that one factor that will affect the observed phase behavior is the aggregation number of the associating polymers. In this work, the aggregation number is constant and has been assumed to be 6 during the theoretical calculations. One way of affecting the number of AT chains within an aggregate is to add a low molecular weight surfactant such as sodium dodecyl sulfate.[17] The addition of such compounds has been shown to produce profound changes in their rheology, which can be accounted for by considering the changing aggregation number of the AT associations.[17] It is speculated that addition of surfactants will thus also dramatically affect the phase behavior of AT/PEG mixtures. Work is in progress on this issue and will be reported shortly.

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