

Application Report

Polymer-surfactant interactions

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Industry section: Chemics
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Force Tensiometer – K12

Method:  

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Surface tensiometry as a technique for the study of polymer/surfactant interactions in solution

Aqueous solutions of non-ionic polymers and non-ionic surfactants

Background

Polymers and surfactants are used in unison in a variety of industrial and commercial systems ranging from cosmetics and detergents to coatings and agricultural sprays. However, in formulating products it is often found that property enhancement is a non-linear function of both the absolute and the relative concentrations of the polymers and surfactants in the system. This is particularly the case in situations where molecular level polymer/surfactant interaction is occurring. Polymer/surfactant interactions are often highly complex, substantially studied and debated, and certainly the key to properties in any number of products. The overall goal in terms of product formulation thus becomes to understand the nature and extent of polymer/surfactant interaction in the system with which you are concerned, and then to gain the ability to manipulate these interactions to produce unique and desirable product properties.

The purpose of this application note is two-fold. The first purpose is to present a fundamental molecular concept of the nature of polymer/surfactant interaction and what it means to system properties. The second is to show in detail, and through the use of an example set of systems, the usefulness of surface tensiometry in quantifying the extent of polymer/surfactant interaction for systems in which both polymer and surfactant are present. As was stated above, polymer/surfactant interaction in solution is a complex and, in certain forums, controversial issue. Volumes have been written on the subject.ⁱⁱ The introduction provided here is by no means comprehensive and Krüss certainly recommends that individuals who are concerned with polymer/surfactant interaction study the relevant literature. In the work presented here the simplest form of polymer/surfactant interaction is discussed- the interaction between a nonionic polymer and a nonionic surfactant in aqueous solution. Krüss plans future application notes pertaining to more complex forms of polymer/surfactant interaction.

In aqueous solution the driving force for nonionic polymers and nonionic surfactants to interact is primarily "the hydrophobic effect".ⁱⁱⁱ The hydrophobic effect is a thermodynamic drive which causes hydrophobic moieties in an aqueous system to aggregate or be expelled. It is caused by the entropic unfavorability of intimate contacts between water molecules and hydrophobic materials. Water molecules which are forced to be intimate with hydrophobes must take on a highly ordered registry in order to compensate energetically for the lack of ability of hydrophobic moieties to hydrogen bond with them.

When a surfactant is in aqueous solution alone the hydrophobic effect causes some fraction of the surfactant molecules (or more precisely their hydrophobic tail groups) to be expelled to the surface of the solution (the air/solution interface). This is physically detectable with surface tensiometry as a decrease in surface tension with increasing surfactant concentration. At some point in surfactant concentration the air/solution interface becomes saturated with surfactant (in terms of chemical potential) and further surfactant concentration increases result in the formation of aggregates of the surfactant in the bulk solution. Such aggregates are commonly referred to as micelles. The concentration at which micelle formation begins is referred to as the surfactant's critical micelle concentration or CMC. Beyond this point in concentration very little further decrease in solution surface tension is measurable since the amount of surfactant adsorbed at the air/solution interface remains essentially constant. Figure 1 depicts the determination of the CMC of an alkyl secondary alcohol ethoxylate having a hydrophobic tail group consisting of an average of 15 alkyl units and hydrophilic head group consisting of an average of 7 ethylene oxide units.

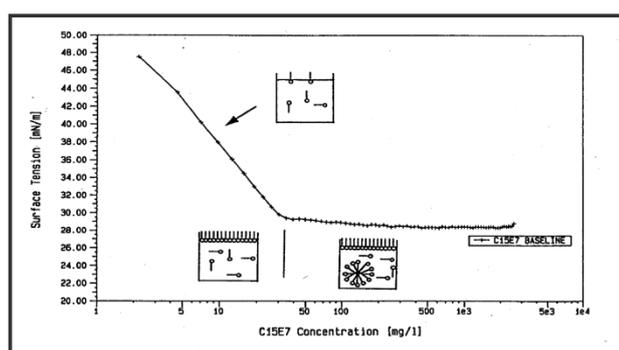


Figure 1

When a surfactant is added to an aqueous polymer solution a third thermodynamic alternative to surface adsorption and self micellization is present for the surfactant. If the polymer has hydrophobic segments then, due to the hydrophobic effect, it can become thermodynamically favorable for the surfactant to adsorb to the polymer and even to form aggregates with the hydrophobic portions of the polymer. Such aggregates are commonly referred to as hemi-micelles.² (If ionic polymers and surfactants are employed then charge-charge interactions between the polymers and the surfactants are

also an alternative, but recall that the focus of this note is nonionic materials. In such systems the main driving force for polymer/surfactant interaction is the hydrophobic effect.)

One of the largest applications of polymer/surfactant interaction in industrial and commercial products is controlled (designed) rheology. Many aqueous based products contain hydrophilic (water soluble) polymers for the purpose of raising the system viscosity and/or causing the product to be properly pseudoplastic (shear thinning) or dilatant (shear thickening). Some of the most important polymers in this regard are hydrophobically-modified water soluble polymers. In other words, hydrophilic polymers which contain hydrophobic segments either pendant to or within the polymer backbone. The rheological character of products containing such polymers is often controlled by the extent to which the hydrophobic effect causes the hydrophobic segments of the polymers to interact. Figure 2 is a schematic representation of the possible effects which hydrophobic modification can have on the behavior of a hydrophilic polymer which is alone in aqueous solution. Please note that, for purpose of illustration, the hydrophobic segments are assumed to be pendants attached to the polymer chains in figure 2. A discussion of hydrophilic polymers with hydrophobic segments in the main chain would be completely analogous.

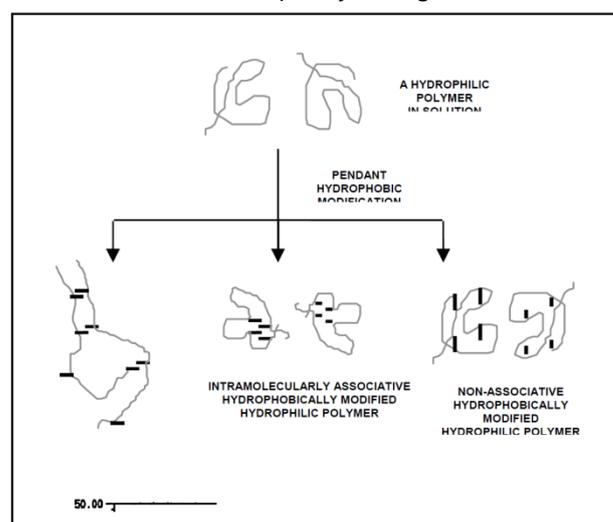


Figure 2

The first possible effect is that hydrophobic modification can cause the polymer to intermolecularly associate in aqueous solution due to the hydrophobic effect forcing hydrophobe/hydrophobe interactions. Polymers which associate in this manner are commonly referred to as "associative thickeners". However, "associative rheology modifiers" may be a better term for them, since they often not only viscosify aqueous solutions but also impart yield stresses and non-Newtonian behavior. The second possible effect is that hydrophobic modification can cause intramolecular polymer association and even insolubility. This tends to decrease the hydrodynamic size of the polymer (compared to its non-hydrophobically modified analogue) and so is not typically desirable if the polymer is

be used as a rheological modifier. The third possible effect is that the hydrophobic modification is not substantial enough, either in terms of the size of each hydrophobe or in terms of number of hydrophobes attached to each polymer chain, to provide either of the first two effects significantly.

Regardless of which of the three situations described above applies to a particular partially-hydrophobic hydrophilic polymer when it is alone in aqueous solution, the presence of surfactant can alter the situation dramatically. As was stated previously, for nonionic polymer/nonionic surfactant situations it may be thermodynamically favorable for interaction to occur between the hydrophobes of the polymer and the tail groups of the surfactant. Figure 3 shows the effects of nonionic polymer/nonionic surfactant interaction in schematic form.

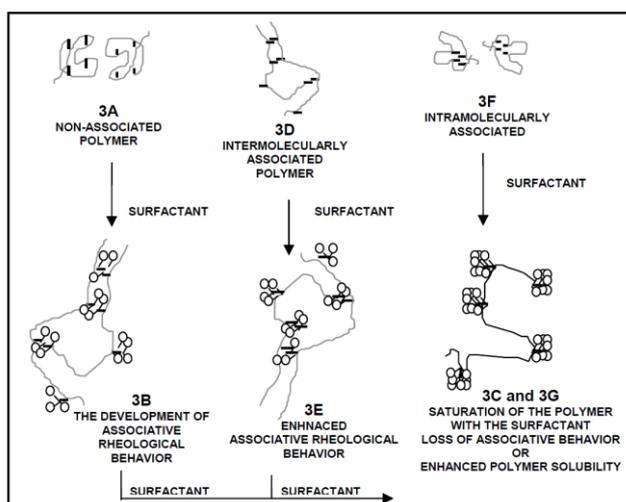


Figure 3

For a polymer which is partially hydrophobic, but still predominately non-self-associating when it is alone in aqueous solution (see schematic 3A), the presence of surfactant can cause the development of associative type rheological behavior. The reason that this is thermodynamically favorable is that even when the polymer is in solution alone the hydrophobes are still driven to associate by the hydrophobic effect. However, the hydrophobes are not of substantial enough size (or there are not enough of them attached to the polymer) for association to become thermodynamically favorable. The opposing and overriding thermodynamic consideration is that the polymer itself would need to lose conformational entropy in order to associate. Surfactant, however, can be driven by the hydrophobic effect to interact with the hydrophobes of the polymer. This interaction provides for a set of hydrophobes on the polymer which each consist of the one original (chemically bound) hydrophobe and one or more physically bound surfactant tails. These composite hydrophobes have a greater hydrophobicity and are, therefore, more strongly driven to associate by the hydrophobic effect. In situations where this thermodynamic drive more than compensates energetically for the lost in entropy associated with intermolecular polymer interaction

a system with associative rheological behavior will be established due to the interaction of the surfactant and the polymer (see schematic 3B). This is rheological behavior that could not be established with either the polymer or the surfactant alone.

Once an associative polymer/surfactant network is established further surfactant addition may or may not (depending on the particular system) lead to enhanced network formation. In many cases the interactive network will reach a maximum in terms of yield stress or elastic modulus with increasing surfactant concentration. If surfactant concentration is further increased there begins to be enough surfactant available for each hydrophobe on the polymer to be saturated with surfactant molecules (surrounded by its own hemi-micelle). At this point there is no further thermodynamic advantage to polymer intermolecular association, since the polymer chains can take on a less entropically restricted near random coil conformation with their hydrophobes solubilized in micelle-like aggregates (see schematic 3C). The associative rheological properties of the system are generally lost at this point.

For a polymer with hydrophobes that intermolecularly associate in the absence of surfactant (schematic 3D), surfactant molecules can interact with the hydrophobes which are involved in the intermolecular polymer associations. They can also promote the establishment of further associations between non-associated polymer hydrophobes, in the same manner as has been described above for the situation in which the polymer does not associate extensively in the absence of surfactant. In both cases the result can be enhanced associative rheological behavior (increased system yield stress, and viscous and/or elastic modulus) because the surfactant molecules act as a "glue" for the association of hydrophobic polymer segments.

In thermodynamic terms, the system free energy increase due to the disassociation of a union of two intimate polymer hydrophobic segments is greater when a number of surfactant molecules are also intimately associated with that union. More kT energy is necessary to disassociate a union and expose two polymer hydrophobic segments and a number of hydrophobic surfactant tails to the surrounding water structure compared to the kT energy required to disassociate a union consisting of only two hydrophobic segments. On the subject of the disassociation of hydrophobe/hydrophobe interactions in aqueous solution, it should be stated that such interactions are dynamic in nature. For purposes of representing these interactions schematically only the lowest energy state (interaction) is portrayed. However, in reality the interactions are constantly disassociating and reforming. The relative amount of time which the hydrophobes spend in each state (disassociated versus associated) depends on the ratio of the kT energy of the system to the free energy of association. Therefore, enhanced associative properties

(schematic 3E) are technically due to the association of surfactant molecules at unions between polymer hydrophobic segments causing the absolute value of the free energy of formation of the unions to increase. This increases the percentage of time that each union is intact, which in turn makes the system act more like an associated (or crosslinked) network rheologically. However, while a moderate amount of surfactant may enhance associative behavior, increasing surfactant concentration further can actually cause the system to lose its associative rheological properties (see schematic 3C). This is analogous to the situation described previously for polymers which do not significantly intermolecularly interact in the absence of surfactant.

In the case of a hydrophobically modified water soluble polymer which tends to intramolecularly associative when it is alone in aqueous solution (schematic 3F) the interaction of surfactant molecules with the associating hydrophobes can also cause a number of results. Tighter association and even polymer/surfactant complex insolubility or phase separation can result. At higher surfactant concentrations solubility, due to hemi-micelle formation, may also occur (schematic 3G). Some polymers are actually only soluble in the presence of very low and very high concentrations of surfactant. At intermediate concentrations of the same surfactant they phase separate.

Just from this brief introduction to polymer/surfactant interaction reasons why system properties are often not simple functions of component concentrations should have become apparent. The power of understanding the polymer/surfactant interactions which are occurring in your system should also be beginning to become evident. Now the question is, "What techniques can be used to identify and quantify polymer surfactants interactions in solution?" Traditionally, rheology has been used and as a stand-alone technique, and it is probably the most important technique. By studying the elastic and viscous components of viscosity and shear modulus for polymer/surfactant systems one can: (1) identify if the polymers and the surfactants in the system interact, (2) narrow in on the proper surfactant/polymer combinations and relative concentrations necessary to produce certain properties in the system, and (3) even get an idea of the actual extent of physical (hydrophobe/hydrophobe) crosslinks in the associative systems as a function of surfactant concentration.^{iv} Rheology is also most useful in that, well it may not provide specific molecular level system information, its quantitation of system properties is often directly applicable to actual product use.

However, rheological studies of polymer/surfactant interaction do have several disadvantages. One of the most serious disadvantages, scientifically, is that in working in the range of surfactant concentrations above the surfactant's CMC it is often difficult to know if the rheological properties which the system is exhibiting are due to polymer/surfactant interaction or to the formation of

various surfactant crystalline mesophases. Of course an extensive set of control experiments may assist in this regard, but that leads to a second disadvantage. If one wants to know to what extent a given polymer and a given surfactant interact, where does he or she begin rheological studies in terms of relative and absolute concentrations? With rheology alone there is no way to know, except trial and error and experience (if you are lucky enough to have some experience that is relevant). The final disadvantage of rheology, to be noted here, is its possible non-relevance to the actual use of the system of interest. In the last paragraph the relevance of rheology to the end use of the system of interest was cited as an advantage of rheology. This apparent contradiction is due to the most common application of polymer/surfactant interaction being rheological modification. Indeed the introduction to polymer/surfactant interaction provided in this text has focused on this application. However, there are numerous other applications of polymer/surfactant interaction in which system rheology is not the most relevant feature. For example, hydrophobically-modified hydrophilic polymers are used in waste water cleanup. The goal is to use the polymer to trap (complex with) surfactants and other amphiphilic moieties thereby eliminating them from the bulk water. In this application the amount of amphiphile trapped per unit polymer is important, but system rheology is of minor interest.

Given the limitations of rheology, one of the best and most facile ways to begin detailed studies of polymer/surfactant interaction is surface tensiometry. Surface tensiometry, as we shall see, overcomes many of the disadvantages of rheology as a scientific technique for systems in which the extent of polymer/surfactant interaction is initially unknown. Surface tensiometry can be used to quickly quantify the extent of interaction between a polymer and a surfactant in solution and to narrow down the range of polymer and surfactant concentrations that may be of interest for further investigation by rheological and other techniques.

At the beginning of this note the fact that polymer in solution provides a third alternative to the water structure, in terms of opportunities to diminish water/surfactant tail interactions, was discussed. The surfactant can be driven to associate with the polymer (particularly the hydrophobic portions of the polymer). Whether or not such an alternative becomes extensively favorable, in terms of thermodynamics, depends largely on the molecular structure of not only the polymer, but the surfactant as well. Also recall that the use of ionic polymers and surfactants increases the number of thermodynamic alternatives to an even greater extent. Such considerations, based on specific polymer and surfactant molecular architectures, are left to future efforts. For now suffice to say that not every partially-hydrophobic hydrophilic polymer in aqueous solution will interact with every surfactant. In fact polymer/surfactant pairs that do not interact are the rule rather than the exception. That is, of

course, the reason why the properties of polymer/surfactant systems wherein the polymers and surfactants do interact are unique. It is also a strong reason to begin any detailed study to polymer/surfactant interaction with surface tensiometry which will indicate in a few simple experiments if the polymer/surfactant pair of interest does in fact interact.

Figure 4 indicates graphically how surface tensiometry can be used as a method to quantify polymer/surfactant interaction. The figure contains two hypothetical surface tension versus surfactant concentration curves. The dashed curve is a typical CMC for a surfactant alone in aqueous solution. The solid curve is a CMC curve for the same surfactant in the presence of a constant aqueous phase concentration of a polymer. It has been assumed that polymer/surfactant interaction is thermodynamically favorable in this hypothetical case. The shape of the solid curve is explained by the numbered cartoons below the graph and the following discussion.

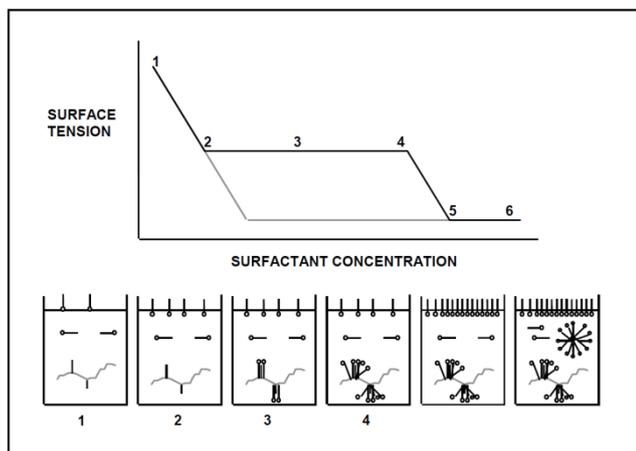


Figure 4

As surfactant is added to the polymer solution it adsorbs at the air/water surface and decreases surface tension (between positions 1 and 2 on the graph). At some point in surfactant concentration (and, therefore, extent of saturation of the air/solution surface by the surfactant) it becomes more thermodynamically favorable for the surfactant to be adsorbed to the polymer versus being continually expelled to air/water interface. This is point 2 on the solid curve which has been termed the "critical aggregation concentration" for the polymer/surfactant pair or simply the CAC.² Beyond this point in surfactant concentration the surface tension of the solution is relatively independent of increases in surfactant concentration for some interval (from point 2 to point 4 on the solid curve). Throughout this interval the surface tension is greater than that of post-CMC concentration solutions of the surfactant alone. The concentration of the surfactant at the air/water interface, which is termed the "surface excess concentration"^v remains relatively constant throughout the interval, while added surfactant is adsorbed onto the polymer. This is why the surface tension remains constant.

As will be seen in the experimental section, wherein actual data is presented for the interaction of hydroxyethylcellulose polymers with an alkyl alcohol ethoxylate, the CAC (point 2) for real systems is seldom found to be a distinct point. The lack of a distinct CAC can be largely attributed to the fact that even the most carefully designed hydrophobically modified polymers have a distribution of extent of hydrophobic modification as well as a molecular weight distribution. The CAC thus becomes a distribution of points pertaining to a distribution of polymer molecules. The most hydrophobic portions of the polymer chains, or the most hydrophobic chains in general, are the first to begin to compete with the air/water interface for surfactant adsorption. Impurities in the surfactant can have a similar effects. Therefore, in a real systems the solid curve of figure 4 typically exhibits parabolic curvature in the region of point 2 instead of a distinct change in slope at point 2.

As the surfactant concentration increases, the polymer eventually becomes saturated with surfactant (point 4 on figure 4). Beyond this point further increases in surfactant concentration serve to increase the air/solution surface excess concentration. Therefore, surface tension again begins to decrease with increasing surfactant concentration. Theoretically, the thermodynamic drive for surfactant adsorption to the air/solution interface will be the same after saturation of the polymer with the surfactant as it was before polymer/surfactant interaction began. As a result, the slope of the surface tension versus surfactant concentration plot between points 4 and 5 should be the same as the slope between points 1 and 2. Point 5 of the solid curve of figure 4 is the critical micelle concentration for the surfactant in the presence of the polymer. At this point both the polymer and the air/solution interface are saturated with surfactant, in terms of chemical potential, and surfactant micelle formation becomes thermodynamically favorable. The surface tension at point 5 is generally the same as its post-CMC value in the absence of the polymer. Further increases in surfactant concentration result in micelle formation.

Three basic pieces of information about the interaction of a polymer and a surfactant can be gained from surface tensiometry work such as that represented theoretically in figure 4. None of these pieces of information are straightforwardly obtainable with rheological studies. Further, with proper surface tension equipment and properly designed experimentation, all are obtainable by a single researcher in about two working days. The three basic pieces of information are:

1. Whether or not the polymer and the surfactant under study do actually interact in solution on the molecular level
2. If they do molecularly interact, the range of polymer to surfactant concentration ratios that will more likely provide for system enhanced rheological properties

3. A quantitative interpretation of the total amount of surfactant that will be associated with a specific amount of polymer at saturation (and even the quantity of associated surfactant per polymer chain or per unit hydrophobic segment if the polymer's molecular architecture is well known)

These basic pieces of information can be obtained from surface tensiometry for an extensive range of polymer/surfactant combinations. This note has been restricted to the discussion of nonionic polymer/surfactant pairs in aqueous solution in order to restrict the initial overview to a discussion of hydrophobe/hydrophobe interactions in aqueous solution. However, surface tensiometry can certainly be applied to systems of ionic polymers and surfactants and to other solvent systems as well. The molecular nature of the interactions between the polymers and the surfactants may change, but the techniques would be the same. With that stated, let it also be stated that some restrictions do apply. The use of surface tensiometry to study polymer/surfactant interaction will certainly become more complicated, and may or may not be possible, in situations where the "polymer" is more surface active than the "surfactant". Such situations are rare, but they do exist. The use of surface tensiometry to study polymer/surfactant interaction in non-polar solvents is also restricted by the fact that the surface may not reflect what is happening in the bulk. In general, if it is impossible to determine the CMC of the surfactant of interest in a particular solvent, then it will certainly be impossible to study the interaction of that surfactant with a polymer in the same solvent. The most widely studied systems are aqueous, however, and for aqueous systems these restrictions rarely apply.

With this background it is now instructive to demonstrate the utility of surface tensiometry in studying polymer/surfactant interaction by discussing a real set of systems. That is the subject of the remainder of this note. The following section briefly discusses the materials and experimental design which were used to investigate the interaction of two cellulose based polymers with an alkyl secondary alcohol ethoxylate nonionic surfactant. The Results and Discussion section includes detailed calculations of the amount of surfactant associated with each polymer, and further discusses the three basic pieces of information that can be obtained for these real systems.

Experimental

The structures of the two polymers and one surfactant used in these experiments are shown in figure 5.

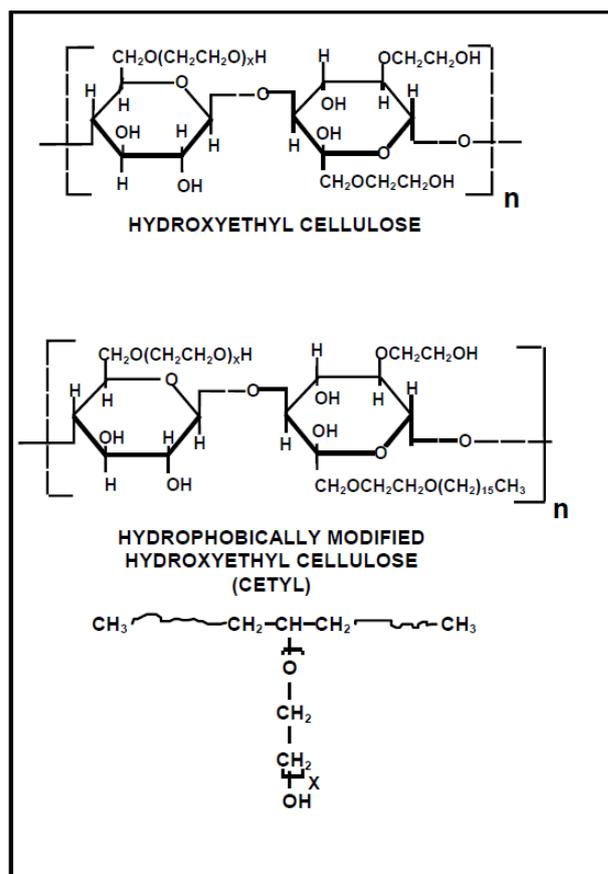


Figure 5

The hydroxyethylcelluloses are both commercially available and of approximately 400,000 molecular weight.^{vi} The hydrophobically modified version of the polymer is reported to contain hydrophobic modification to the extent of 1 cetyl hydrophobe per every 33 anhydroglucose units of polymer chain.^{vii} The surfactant is also commercially available and is an alkyl secondary alcohol ethoxylate. The alkyl tail group of the surfactant has an average length of 15 carbons. The ethylene oxide head group of the surfactant has an average length of 7 units. For simplicity the surfactant will henceforth be referred to as C_{15}E_7 while the polymers will be referred to as HEC and HMEC for hydroxyethylcellulose and hydrophobically modified hydroxyethylcellulose, respectively.

For the surfactant alone in aqueous solution the CMC at room temperature has been determined to be 31.6 mg/L by surface tensiometry. This work was performed using a Krüss model K-12 processor tensiometer. The K-12 was equipped with an automated dosing accessory so that surfactant concentration was incremented automatically. An aqueous dosing solution at a concentration of 5000 mg/L was used and the initial solution was pure distilled water. The Wilhelmy plate technique using a platinum plate was employed. The surface tension versus concentration curve for the C_{15}E_7 , which was used to determine the surfactant's CMC in pure water, is the example curve shown in figure 1. A CMC curve of this type is generated by the K-12 running in the automated dosing mode in about 2 hours. This is a 75 point CMC curve. Less time is, of course,

necessary for a CMC curve with fewer data points and this can certainly be selected. Typical CMC determination can be done accurately with 20 to 25 points. However, since the CMC curve of C₁₅E₇ acts as the base line for the polymer surfactant interaction experiments, detail is desirable.

Figure 6 represents similar work performed on both HEC and HMHEC when each is alone in solution. The K-12 with the automated dosing accessory and the Wilhelmy plate technique was again employed. The aqueous polymer dosing solutions were 4000mg/L HEC and 4000mg/L HMHEC, respectively, for the two runs. The initial solution was again pure distilled water. Since the purpose of these experiments was simply to make sure that the polymer was not more surface active than the surfactant 40 point curves were sufficient in each case. Total instrument time was 3 hours to generate both sets of data.

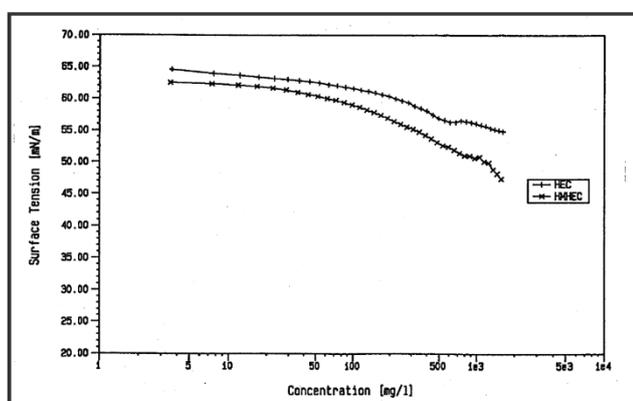


Figure 6

The data represented in figure 6 indicates that neither polymer is substantially surface active as compared to the C₁₅E₇, so that polymer surfactant interaction studies on these systems using surface tensiometry will be facile. It is interesting to note that HMHEC is somewhat more surface active than HEC due to its hydrophobic modification. This, of course, displays another application of surface tensiometry- characterization of the surface activity of water soluble polymers, and therefore of their extent of hydrophobicity.

Following these background experiments four polymer/surfactant interaction experiments were performed. These experiments can be thought of as CMC experiments for C₁₅E₇ in aqueous polymer solutions. Such experiments are most straightforwardly run under conditions of constant aqueous phase polymer concentration with surfactant concentration being incremented. Using the automated K-12 processor tensiometer, this requires the use of an initial solution which contains the polymer at the concentration of interest, and a dosing solution which has both a high concentration of surfactant and a concentration of polymer equal to that of the initial solution. If such stock solutions are used, then incremental additions of the dosing solution will increase the surfactant concentration in the system and leave the polymer concentration constant. Using this technique, surface tension versus surfactant concentration data was taken for C₁₅E₇ in the presence of two concentrations of HEC and two concentrations of HMHEC. Each aqueous dosing solution had a C₁₅E₇ concentration of 5000mg/L in addition to the proper concentration of polymer. Each initial aqueous solution contained no surfactant and the concentration of polymer of interest. The polymer concentrations studied were 100mg/L HEC, 2000mg/L HEC, 100mg/L HMHEC, and 2000mg/L HMHEC. Each of the four experiments required approximately 2 hours of instrument time.

Results and discussion

Studying first the results for the unmodified hydroxyethylcellulose polymer (HEC), it can be observed from figure 7 that HEC, even in the absence of hydrophobic modification, has enough hydrophobicity to interact with C₁₅E₇. In the absence of polymer/surfactant interaction the CMC curve for the C₁₅E₇ in the presence of any concentration of the polymer would be no different from the CMC curve for the surfactant alone in solution. In other words, the surfactant would saturate the air/solution interface and then begin forming micelles at the same concentration regardless of the presence of the polymer.

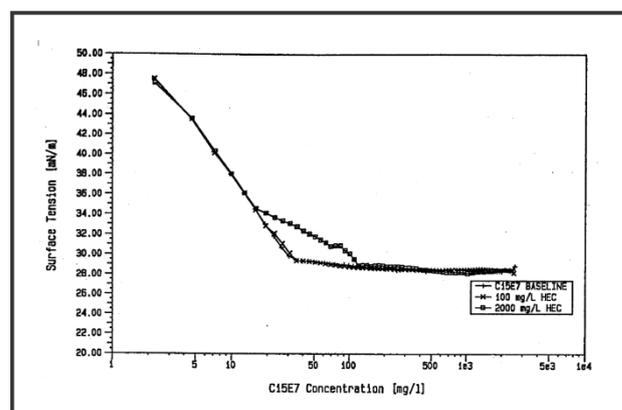


Figure 7

The figure 7 results indicate that the CMC of C₁₅E₇ in the presence of 2000mg/L of HEC is 125mg/L. This indicates that for a 2000mg/L solution of HEC, the polymer, as well

as the air/solution interface, is saturated with $C_{15}E_7$, in terms of chemical potential, once the $C_{15}E_7$ concentration reaches 125mg/L. By simply subtracting the 31.6mg/L of $C_{15}E_7$, that a CMC study of the surfactant alone indicates is necessary for the surfactant to saturate the air/solution interface prior to micelle formation, from 125mg/L, it is calculated that 93.4mg/L of $C_{15}E_7$ is necessary to saturate the 2000mg/L of HEC. Put more simply 93.4mg of $C_{15}E_7$ associates with every 2000mg of HEC in aqueous solution. However, it is also known that the molecular weight of $C_{15}E_7 \approx 530\text{g/mole}$ and the molecular weight of a single anhydroglucose along the HEC backbone $\approx 196\text{g/mole}$. Using this information, and the fact that HEC is purely repeat anhydroglucose units, it can be easily calculated that 1.73×10^{-2} moles of $C_{15}E_7$ associate with every mole of anhydroglucose units contained in the backbones of the HEC chains at saturation. Put more simply 1 molecule of $C_{15}E_7$ complexes with every 57.9 anhydroglucose backbone units of the HEC. This is certainly not a great deal of association and in no way indicates that aggregates of the size which could be considered hemi-micelles form on the HEC backbone.

Note that, as expected, the CAC for this polymer surfactant combination was not readily apparent from the 2000mg/L HEC experiment. Rather than being a distinct point where the surface tension as a function of surfactant concentration data in the presence of the polymer deviates from the trend of the CMC data for $C_{15}E_7$ alone in solution and simultaneously takes on a zero slope, the CAC is a range of concentrations. In fact the CAC range extends from approximately 17mg/L to 55mg/L for the 2000mg/L HEC work. As was indicated previously, this phenomena can be largely attributed to the fact that the HEC is actually a distribution of molecules of varying molecular weight and extent of hydrophobicity. This distribution of polymer molecular architectures causes a distribution in the point at which it becomes thermodynamically favorable for HEC to interact with $C_{15}E_7$ molecules.

Studying next the results from the 100mg/L HEC work (figure 7), it is apparent that the presence of 100mg/L of HEC causes very little shift in the CMC of $C_{15}E_7$. The shift is barely significant beyond experimental error. (The experimental error on each surface tension data point reported in this work can be estimated to be $\pm 0.2\text{mN/m}$ based on reproducibility work.) This result is not, however, unexpected based on the 2000mg/L HEC work. For a polymer and surfactant pair which do interact it is expected that the same amount of surfactant is required to saturate each chain (or unit) of polymer regardless of the amount of polymer in the solution. Therefore, the magnitude of the shift in the surfactant's CMC should be linearly dependent on the amount of polymer in the system. The 2000mg/L HEC work indicated that 93.4mg of $C_{15}E_7$ complexes with each 2000mg of HEC at saturation. This indicates that 4.7mg of $C_{15}E_7$ is required to saturate each 100mg of HEC, or consequently that the CMC for $C_{15}E_7$ in a 100mg/L aqueous solution of HEC is expected to be 4.7mg/L greater than the CMC for $C_{15}E_7$ in aqueous solution alone. Knowing

that the CMC of $C_{15}E_7$ in solution alone is 31.6mg/L, the expected CMC for $C_{15}E_7$ in the 100mg/L HEC work is thus 36.3mg/L. Although considerations of experimental error make it somewhat inappropriate to use the 100mg/L data shown in figure 7 to calculate the extent of interaction of $C_{15}E_7$ and HEC in aqueous solution, the data certainly does support the 2000mg/L HEC results in that 36.3mg/L is certainly not an unreasonable interpretation of the CMC of $C_{15}E_7$ under 100mg/L HEC conditions.

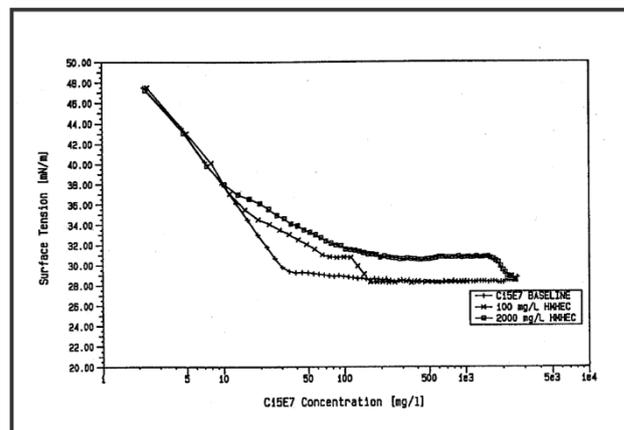


Figure 8

Turning now to the hydrophobically modified polymer (HMHEC), figure 8 shows the results of 100mg/L and 2000mg/L HMHEC work.

As was the case with the HEC work the CAC was found to be a broad transition due to the distribution of polymer molecular architectures that make up HMHEC. The CMC of $C_{15}E_7$ in 2000mg/L HMHEC solution was determined to be 2510mg/L based on this work. This value is substantially greater than the 125mg/L which was found to be the CMC of $C_{15}E_7$ in the presence of 2000mg/L of HEC. The large difference is due to the interaction of $C_{15}E_7$ molecules which the cetyl hydrophobes of the HMHEC. Much more surfactant is required to saturate a given amount of HMHEC versus the same amount of HEC. Further, since HMHEC has been characterized and reported to contain 1 cetyl-modified anhydroglucose unit for every 33 total anhydroglucose units,⁷ and the relevant background studies have been performed on the HEC (which is the analogue to HMHEC without cetyl group attachment), it is possible to calculate the number of $C_{15}E_7$ molecules which associate with each cetyl hydrophobic unit of the HMHEC. In other words, it is possible to calculate the average size of the hemi-micelles which form on the polymer's hydrophobes at surfactant saturation.

In order to demonstrate such a calculation most simply three terms need to be defined:

NGU = an unmodified anhydroglucose unit in the backbone of either HEC or HMHEC, the molecular weight of which $\approx 196\text{g/mole}$

CeGU = an anhydroglucose unit in the backbone of HMHEC which has a cetyl hydrophobe attached to it, the molecular weight of which $\approx 422\text{g/mole}$

GGU = a generic and hypothetical glucose unit chosen from the backbone of an HMHEC polymer chain which could be either a NGU or a CeGU, the molecular weight of a GGU is thus the weighted average of the molecular weights of NGU and CeGU units or $(196 \cdot 32/33 + 422 \cdot 1/33) \approx 203 \text{g/mole}$

Now, from the 2000mg/L HMHEC work it is evident that $2510 - 31.6 = 2478.9 \text{mg}$ of C_{15}E_7 are necessary to saturate 2000mg of HMHEC in aqueous solution. However, 2000mg of HMHEC is, using the definition of GGU provided above, 9.85×10^{-3} moles of GGU's. Further, 1/33 of those GGU's are CeGU's and the other 32/33 are NGU's according to the definitions above. Also, 2478.9mg of C_{15}E_7 is 4.68×10^{-3} moles of C_{15}E_7 . So that 4.68×10^{-3} moles of C_{15}E_7 are necessary to saturate 2.99×10^{-4} moles of CeGU's and 9.56×10^{-3} moles of NGU's. However, considering that HEC is purely NGU units, it is known that 1.73×10^{-2} moles of C_{15}E_7 saturate every 1 mole of NGU units from the work on HEC. Taking this into account allows it to be calculated that, for the 2000mg/L HMHEC work, 4.51×10^{-3} moles of C_{15}E_7 complex with each 2.99×10^{-4} moles of CeGU's. In other words, 15.1 molecules of C_{15}E_7 are associated with each cetyl hydrophobic group of the HMHEC at saturation. An aggregation of surfactant molecules this large on one position of the polymer would certainly be considered a hemi-micelle.

Figure 8 also indicates that in a 100mg/L solution of HMHEC the CMC of C_{15}E_7 is 150mg/L. This result can be also be used to calculate the average number of surfactant molecules in a hemi-micelle which surrounds the cetyl hydrophobe of the HMHEC at saturation. The calculation is analogous to the one described above for the 2000mg/L work and the result should be the same also. The actual result of the calculation is that 14.4 molecules of C_{15}E_7 surround each polymer hydrophobe at saturation. The agreement between this result and the result of 15.1 from the 2000mg/L HMHEC work is quite good. Of course more experiments at variable polymer concentrations for both the hydrophobically modified polymer and the control polymer might be expected to help specify this aggregation number even more closely.

Summary

This application note has served several purposes. It has provided an introduction to polymer/surfactant interaction in solution with particular focus on the purely hydrophobic interactions between nonionic polymers and surfactants in aqueous solution. The majority of the introductory material focused on one of the largest applications of polymer/surfactant interactions in solution- this being designed system rheology. It was pointed out that while rheology has traditionally been, and will continue to be, the foremost technique in the study of polymer/surfactant interaction, rheological techniques do have their disadvantages in this regard. These disadvantages include

the necessity to perform a large number of experiments just to construct a region of interest in terms of the relative concentrations of polymer and surfactant necessary to provide system properties, and the further inability of rheological studies to identify quickly if a particular polymer/surfactant set does in fact interact on the molecular level. The note goes on to discuss the use of surface tensiometry which can be used to: (1) rapidly screen a polymer/surfactant pair to determine if they interact on a molecular level, (2) rapidly bracket the range of polymer and surfactant relative concentrations that should be studied if unique rheological properties are the application, and (3) quantitatively indicate the amount of surfactant which a polymer will adsorb at saturation. Result (3) in particular is useful not only in the formulation of products for rheological applications but also for applications such as the treatment of waste water in which the goal is to use the polymer as a "trap" for surfactants and other amphiphilic moieties. Lastly, example data was presented to justify the use of surface tensiometry in these regards. The interaction between two hydroxyethylcelluloses and an alkyl secondary alcohol ethoxylate was studied. These studies showed that with the use of a Krüss automated tensiometer, and well-designed experimentation, the background data necessary for a further detailed study of properties provided by the interaction of these materials can be gained by a skilled researcher in about two working days.

To end with an analogy, formulating a product in which the properties are dependent on polymer/surfactant interaction and having no idea at what concentrations the interactions, and thus your desired unique properties, will occur is the equivalent of being an alien whose spaceship lands randomly on earth and looking for the President of the United States. If your product application is rheology oriented, as most are, then rheological measurements will allow you to look for the President house by house or square mile by square mile. Surface tensiometry will tell you that the President lives in a big house in Washington D.C. You still need to search, but this makes your job quite a bit easier.

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