

A New Class of Photoresponsive Surfactants

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Abstract—Recently, surface tension has been shown to be important in emerging high technologies, such as in pumping and control of flow in microfluidic devices, in microchemical analysis of complex fluids, and in rapid DNA screening, etc. Advances in these new technologies will depend strongly on the availability of flexible methods for controlling surface tension. Photo-control using a photoresponsive surfactant is a potentially attractive route to accomplishing many of the tasks required in these processes. Photoresponsive surfactants typically incorporate an azobenzene group as the functional unit which experiences reversible trans-to-cis photoisomerization under different irradiation conditions. The photoisomerization usually causes a change in surface tension. Obviously, a large change in surface tension under different illumination conditions will be highly desirable in practical applications. However, the largest change in surface tension as reported in the literature is only 3 mN/m which is too small to generate any significant effect. In this presentation, we report a new class of photoresponsive surfactants which exhibit excellent performance in surface tension control. Under different illumination conditions, the change in surface tension can be as large as 11.0 mN/m. Experimental results are presented for two new photoresponsive surfactants. A discussion of experimental results follows.

Index Terms—azobenzene, nonionic, photoresponsive, surfactant, surface tension control

I. INTRODUCTION

WITH the development of modern technology, manipulation and control of liquids at small length scales, such as the micron and even the nanometer scale, becomes more and more important. One significant example is the need to pump and position liquids in microfluidic networks. Microfluidic networks have great potential for significant applications in bioassays, microreactors, and chemical and biological sensing [1]; but the ability to manipulate fluids at small length scales will be crucial in the

design and fabrication of those devices.

It is usually difficult to precisely manipulate liquids in microfluidic systems. The first difficulty comes from flow resistance. The viscous stress in a fluid is inversely proportional to the system length scale. As a consequence, the flow resistance becomes extremely large at sub-millimeter length scales. The second difficulty is related to surface or interfacial effects. The ratio of surface to volume increases significantly when the length scale of the system is reduced. This results in significant effects of surface properties on liquid behavior. Therefore, fluid movement can be much more complicated in microfluidic networks. One way to overcome those difficulties is to utilize both the small length scale and the surface effect to pump the liquid. The principle behind this idea is the “Marangoni effect”. In a continuous fluid system, if there exists a surface tension gradient at its interface, liquid will flow spontaneously from the low surface tension region to the high surface tension region [2]. In applying the “Marangoni effect” to a microfluidic network, one particular advantage is that the driving force is independent of the length scale. Therefore, the “Marangoni effect” is especially suitable to pump liquids in a microfluidic network.

In order to utilize the “Marangoni effect”, it is important to find a convenient method to control surface tension. There exist several methods by which surface tensions can be actively controlled. Among these methods, photo-control of surface tension is perhaps the most attractive. With the power of modern optical technology, it is not difficult to accomplish flexible photo-control of surface tension with high spatial and temporal resolution. The spatial resolution could be at the order of a micron, while temporal resolution could be several seconds. One prospective method to achieve photo-control of surface tension is to use photoresponsive surfactants [3]. In an aqueous solution of photoresponsive surfactants, surface tension could be changed under different illumination conditions. As a result, the surface tension gradient is easily created by spatially patterned illumination.

Photoresponsive surfactants are usually produced by incorporating a light-sensitive azobenzene group into the surfactant tail. The azobenzene group experiences reversible trans-to-cis photoisomerization under different illumination conditions. Under visible light, azobenzene will take the trans form; under UV light, azobenzene will convert to the cis form (Figure 1). As a consequence, conformation of the photoresponsive tail can be controlled by light. The variation

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in surfactant conformation usually causes a change in surface tension. Because of geometrical factors, the cis surfactant forms a looser adsorbed layer at the surface and has a larger average area per molecule than trans does. The relatively large average area per molecule causes cis surfactants to possess a higher surface tension than trans, because surface tension is normally roughly proportional to average area per molecule.

From the viewpoint of applications, a large surface tension change in the saturated region, i.e. at concentrations well above the CMCs of both the trans and cis forms, is highly desirable. However, the largest change in saturated surface tension as reported in the literature is only 3 mN/m, which is too small to generate any significant effect. We noticed that all reported photoresponsive surfactants have been ionic. The strong electrostatic repulsion between head groups makes these surfactant molecules possess a large average area per molecule. The relatively large average area per molecule may weaken the effect of trans-to-cis conformation change on surface tension.

In this work, we have developed an homologous series of two new, nonionic surfactants, as shown in Figure 2. Experimental results of surface tension for these surfactants are reported under both UV and visible light. A discussion of experimental results follows.

II. EXPERIMENTAL SECTION

The surfactants synthesized were triethylene glycol mono(4-butylazobenzene) ether (C4AzoOC2E2) and diethylene glycol mono(4',4-hexyloxy, butyl-azobenzene) ether (C4AzoOC6E2). Their structures are indicated in Figure 2. The synthesis procedure for these surfactants is described in reference [4]. The molecular structure and purity of all surfactants were verified and analyzed by H1-NMR,

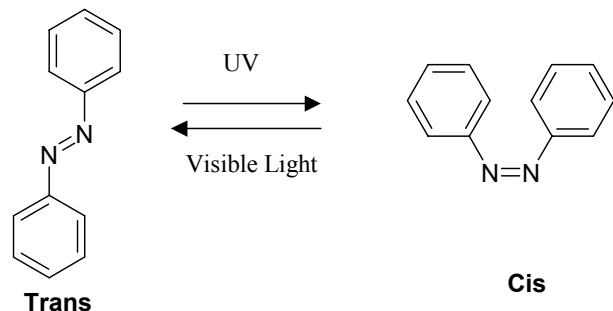


Fig. 1. Photoisomerization of azobenzene.

mass spectrometry (Bruker DALTONICS APEX 3 Tesla, FT-ICR-MS, with Electrospray Ion source), elemental analysis and gas chromatography (GC). The equilibrium surface tension was measured at a temperature of 25 °C with a Krüss K10T tensiometer using the Wilhelmy plate method. A chart recorder was used to trace the surface tension variation with time. UV-VIS absorption spectra were obtained with a Hewlett-Packard HP 8453 spectrophotometer. The light source was a 200W mercury lamp (Oriol 6283) mounted in an

arc lamp housing (Oriol 66902) and powered by an arc lamp power supply (Oriol 68910). The UV light was obtained by using a 320 nm band pass filter (Oriol 59800). A 400 nm long pass filter (Oriol 59472) was utilized to obtain visible radiation.

III. RESULTS AND DISCUSSION

A. UV/VIS absorption properties

Photoisomerization was verified by UV/VIS spectra; typical spectra are shown in Figure 3. Normally, the absorption band in the trans form corresponds to a $\pi \rightarrow \pi^*$ transition, while for cis it corresponds to an $n \rightarrow \pi^*$ transition [5]. Therefore, the absorption wavelength for the trans band is usually shorter than for cis. The maximum absorption wavelengths for trans C4AzoOC2E2 and C4AzoOC6E2 are 343 nm and 325 nm, respectively. The shift in maximum absorption wavelength observed here was probably caused by an increasing steric hindrance with increasing spacer length. In addition, the maximum absorption wavelengths in cis C4AzoOC2E2 and C4AzoOC6E2 are 440 nm and 435 nm, respectively. Under UV illumination, absorption decreases in the trans band; at the same time, absorption grows in the cis band. The observed phenomenon is consistent with trans-to-cis photoisomerization

B. Surface Tension Measurements

Equilibrium surface tensions of all aqueous surfactant solutions were measured as a function of surfactant concentration before and after UV illumination. The results, shown in Figure 4, are consistent with established behavior in that the surface tension initially decreases with increasing concentration but then levels off and does not change with further concentration increases [2]. The concentration at which this abrupt change in slope occurs, and above which the surface tension is constant, corresponds to the critical micelle concentration (CMC). The absence of any dip in the surface tension curve in this region suggests the absence of highly surface-active impurities in the solutions

The surface excess concentration, which is directly related to average area per molecule in adsorbed layer, can be inferred from the slope of the surface tension versus concentration curve. From the Gibbs equation, surface excess concentration, Γ , is calculated from [6]

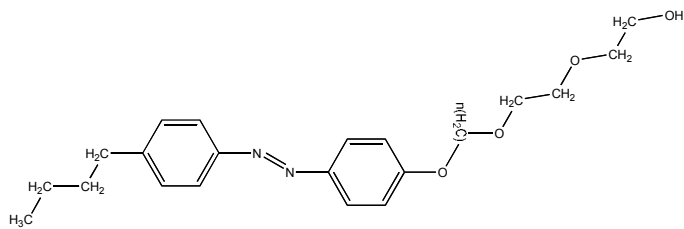


Fig. 2. Molecular structure of photoresponsive surfactants. $n=2$, C4AzoOC2E2; $n=6$, C4AzoOC6E2

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln c} \quad (1)$$

where c is the concentration of surfactant in bulk solution, R is the gas law constant and T the absolute temperature. The area per molecule is obtained simply from the inverse of this surface excess concentration as $A = 1/\Gamma N$, where N is Avogadro's number.

In C4AzoOC2E2, after UV illumination, surface tension increases in the pre-micellar region. However, the change in saturated surface tension is essentially zero. Similarly, surface excess concentration decreases only 3% after UV illumination. These experimental results are important. They demonstrate that simple trans-to-cis conformation change may have little effect on both saturated surface tension and surfactant packing at the interface, even in nonionic photoresponsive surfactants. In C4AzoOC6E2, surface tension in the pre-micellar region can be increased by as much as 19.1 mN/m after UV illumination whereas the largest change reported in literature is 13.6 mN/m. More important, the change in saturated surface tension is as large as 11.0 mN/m, which far exceeds the largest change of 3.0 mN/m reported in the literature. Correspondingly, surface excess concentration decreases significantly after UV illumination. The surface excess concentration for cis is 1.5 times smaller than for trans. These results are really unexpected. A slight variation in molecular structure can cause a drastic change in performance of surface tension control.

It is found from these experimental results that surface tensions in the saturated region are roughly inversely proportional to surface excess concentration. The saturated surface tension is usually large for a small surface excess concentration; but for a large surface excess concentration, the saturated surface tension is small. Because surface excess concentration is directly related to surfactant conformation at the interface, these experimental results imply that a large

conformation change might be responsible for the observed large change in saturated surface tension. This large conformation change cannot be explained merely by the trans-to-cis conversion. As we already know, simple trans-to-cis conformation change has little effect on the surfactant packing at interface. However, the middle polar group (ether oxygen) could drive the surfactant to produce a secondary conformation change. Because of the middle polar group, surfactant molecules potentially can take two kinds of conformation at the interface. The first one is simply a vertical conformation in which the head group is immersed into water and the tail group stands out toward the air. The vertical conformation is stabilized by strong $\pi - \pi$ interactions between azobenzene groups. The second conformation is a "loop" conformation. In the "loop" conformation, the middle polar group is in contact with water and the spacer will loop out from the interface. This conformation is stabilized by a hydrogen bond between the middle polar group and water. In C2AzoOC2E2, the spacer is too short to permit the surfactant to take the "loop" conformation. Both trans and cis surfactants take a vertical conformation at the interface. The average areas per molecule are almost the same. As a result, the saturated surface tension changes little after UV illumination. In C4AzoOC6E2, the longer spacer provides much greater flexibility. Cis surfactant therefore can take the "loop"

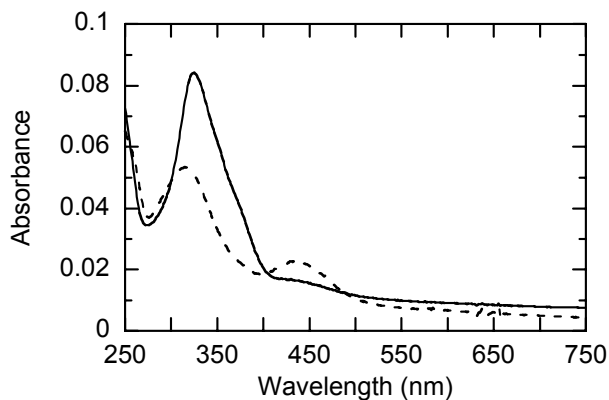


Fig. 3. UV/VIS absorption spectra of C4AzoOC6E2 at both trans state (solid line) and cis state (dash line).

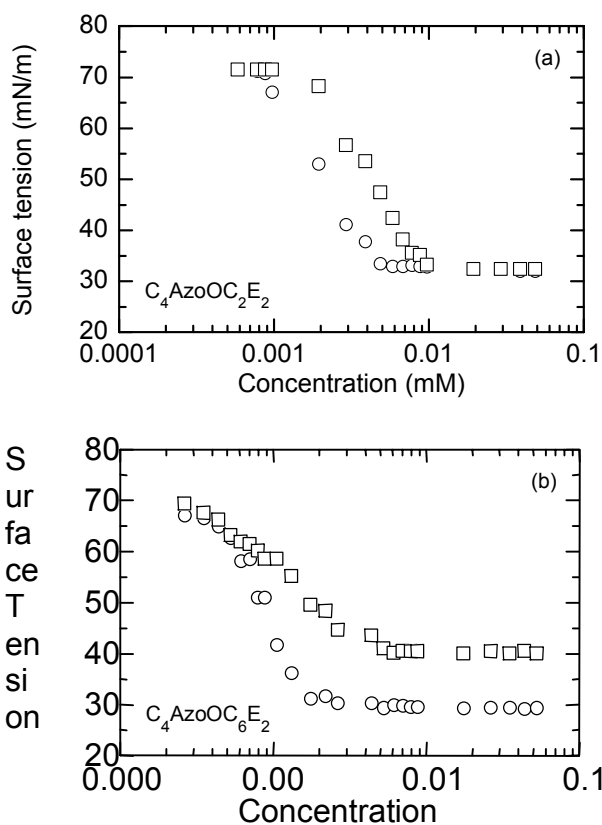


Fig. 4. Equilibrium surface tensions of (a) C4AzoOC2E2 (b) C4AzoOC6E2 state (dash line).

conformation. However, the flexibility is not sufficient to allow trans surfactant to take the “loop” conformation. Therefore, there is a large change in average area per molecule between trans and cis surfactants. Correspondingly, the change in surface tension is large.

IV. *CONCLUSIONS*

We have reported on the synthesis and characterization of a new class of nonionic, photo-sensitive surfactants, some of whose trans and cis isomers exhibit unusually large differences in surface properties. For example, the change in saturated surface tension is as high as 11.0 mN/m. The surface tension in the pre-micellar region can increase by as much as 19.1 mN/m by UV illumination. Experimental results show the important role of the middle polar and azobenzene groups in the control of surface tension and surfactant conformation at the interface.

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