Evidence for Synergism in Nonionic Surfactant Mixtures: Enhancement of Solubilization in Water-in-Oil Microemulsions

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It is well-known that certain mixtures of surfactants can provide better performance than pure surfactants for a wide variety of applications, and thus it is expected that enhanced solubilization of water in water-in-oil (w/o) microemulsions will also be achieved with certain surfactant mixtures. The formation of w/o microemulsions involves dissolving an aqueous phase into an oil phase, creating a transparent and thermodynamically stable suspension of droplets with diameters in the range of 10–100 nm. It is desirable to accomplish this with a minimum amount of surfactant, and in order to achieve this goal, mixtures of surfactants can be used. We intend to address different surfactant mixtures that exhibit synergism in the solubilization of water in w/o microemulsions, showing the existence of at least two different mechanisms of synergism.

Synergism in surfactants may be defined as any situation where mixtures of surfactants have superior properties when compared to the properties of any of the single components alone. Although certain mixtures of dissimilar surfactants can be expected to show synergism, enhancement in properties may also occur with mixtures of similar structures. Shinoda et al. have demonstrated that macroemulsions made with nonionic surfactants that have been purified to a single poly(ethylene oxide) chain length are generally less able to solubilize the dispersed phase into the continuous phase, when compared to macroemulsions made with surfactant having the same average length, but an ethylene oxide size distribution. Ordinarily, one would not expect strong synergistic effects in mixtures of nonionic surfactants, as synergism in anionic/nonionic surfactant mixtures has been attributed to Coulombic, ion–dipole, or hydrogen-bonding interactions among the polar groups. Nonionics, which have minimum intermolecular interactions, should have, by comparison, the lowest synergism of all mixtures. In light of this previous work, we are able to demonstrate strong synergism in nonionic surfactant mixtures.

When formulating water-in-oil microemulsions, one must account for several factors, including the partitioning of the surfactant (or its components) between the oil, water, and interfacial domains (Figure 1). For maximum solubilization it is desirable to have most of the surfactant at the interface between the oil and water, rather than dissolved in the oil or water phases. Increasing the interfacial area should also increase solubilization. Synergism in microemulsion solubilization has been previously reported for a nonionic–anionic system designed for pharmaceutical applications, using mixtures of AOT (sodium bis(2-ethylhexyl)sulfosuccinate) and Arlacel 20 (sorbitan laurate) in different proportions. The present paper reports similar improvements using nonionic–nonionic surfactant mixtures for solubilization of water in water-in-oil microemulsions and provides evidence for two different synergism mechanisms.

**Experimental Procedure**

Microemulsion solubilization experiments were performed by titrating water into a mixture of surfactant and oil. The transition from a clear to a cloudy solution indicates that the maximum water solubilization has been exceeded. The rate of solubilization decreases as the maximum solubilization is approached. Due to these kinetic considerations, the final cloudy transition was established only after several hours of stirring of a sample. All experiments were performed at 25 °C. The initial surfactant to oil ratio was 0.20 by weight, with nonylphenyl ethoxylate surfactants (Igepal CO series, Rhone-Poulenc, Cranbury, NJ) and cyclohexane (Fisher Scientific, Fair Lawn, NJ) as the oil phase. Similar microemulsions have been well-characterized and used for nanoparticle synthesis.

The surfactants used in the solubilization experiments are commercial grade nonylphenyl ethoxylates (C₉H₁₉C₆H₄(OC₂H₄)ₙOH), with properties summarized in Table 1. This family of surfactants has the same hydrophobic domain (nonylphenol) and variation only in the length of the hydrophilic domain, which consists of poly(ethylene oxide). No attempt was made to further purify these materials. These surfactants are synthesized by polymerization of ethylene oxide to nonylphenol, resulting in a wide distribution of the number of ethylene oxide residues on any given molecule, around an average EO number for the mixture.

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Table 1. Surfactants Used in This Studya

<table>
<thead>
<tr>
<th>surfactant (Igepal)</th>
<th>abbrev</th>
<th>EO number</th>
<th>HLB</th>
<th>water soluble</th>
<th>oil soluble</th>
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<tr>
<td>CO-210 C₉PhE₁,₅</td>
<td>1.5</td>
<td>4.6</td>
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<td>yes</td>
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<tr>
<td>CO-430 C₉PhE₄</td>
<td>4</td>
<td>8.8</td>
<td>no</td>
<td>yes</td>
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<tr>
<td>CO-520 C₉PhE₅</td>
<td>5</td>
<td>10.0</td>
<td>no</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>CO-530 C₉PhE₆</td>
<td>6</td>
<td>10.8</td>
<td>no</td>
<td>yes</td>
<td></td>
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<tr>
<td>CO-610 C₉PhE₇,₅</td>
<td>7.5</td>
<td>12.2</td>
<td>yes</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>CO-720 C₉PhE₁₂</td>
<td>12</td>
<td>14.2</td>
<td>yes</td>
<td>yes</td>
<td></td>
</tr>
</tbody>
</table>

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The distribution of these chain lengths is often assumed to be a Poisson distribution and may also include a few percent unreacted nonylphenol or material with EO = 1 or EO = 2 in excess of that predicted by the Poisson calculation. All surfactants were soluble in cyclohexane, and only the two with the largest EO number were soluble in water. It is expected that the surfactants with lower EO number are more oil soluble, especially in n-alkane oils.

Solubilization results are presented as a maximum water-to-oil volume ratio ($x_{solubilized}$). To convert to weight fractions of water ($W$), oil ($O$), and surfactant ($S$), the following formulas may be used, based on sample sizes of 1.2 g of surfactant and 4.8 g of oil (6.16 mL for cyclohexane).

\[
W = \frac{6.16x}{(6 + 6.16)x}
\]
\[
O = \frac{4.8}{(6 + 6.16)x}
\]
\[
S = \frac{1.2}{(6 + 6.16)x}
\]

The maximum solubilization of 0.44 water/oil volume ratio for the optimum C$_9$PhE$_{1.5}$/C$_9$PhE$_{12}$ case represents a total of 31 wt % water, 55 wt % oil, and 14 wt % surfactant, or a 0.56 water/oil weight ratio.

**Discussion**

Figure 2 shows water solubilization in water-in-oil microemulsions for single nonylphenyl ethoxylates, as well as binary mixtures, vs HLB. The HLB can be calculated for these surfactants from the average EO content of the molecule. HLB is defined as the hydrophile–lipophile balance of a surfactant, and for ethoxylated surfactants can be calculated as 20 times the weight fraction of polyethylene oxide (ethylene oxide) in the molecule.\(^\text{10,11}\) HLB was initially intended to aid in the selection of surfactant mixtures for microemulsion formulation.

Of the single surfactants studied, nonylphenyl ethoxylate (C$_9$PhE$_3$), with an HLB of 10.8, achieved the largest solubilization of water in cyclohexane (Figure 2). This system compares favorably with previous water-in-oil microemulsion formulation results using n-alkanes and sorbitan ester ethoxylates,\(^\text{12}\) where it was established that optimum w/o microemulsions were created for surfactant mixtures that fell in the HLB 8.5–11 range. This range is much different from that of macroemulsions, where w/o emulsions are expected to form for surfactant mixtures in the HLB 3–6 range, while o/w emulsions generally form in the HLB 10–18 range.\(^\text{10,11}\)

Two different surfactant mixtures were investigated. Case 1 (Figure 2) involved two surfactants, C$_9$PhE$_4$ and C$_9$PhE$_{7.5}$, that were close in molecular size to C$_9$PhE$_6$, which was the best performing single surfactant. Case 2 (Figure 2) involved C$_9$PhE$_{1.5}$ and C$_9$PhE$_{12}$, which were much less similar in molecular size than the previous case. Both of these mixtures showed superior solubilization results over either pure component at some mixture ratio, with case 2 clearly showing superior results over both case 1 and the best single surfactant case. The underlying reasons for these differences become more clear when we examine the composition of the mixtures.

**Surfactant Size Distributions**

As the surfactants we consider here are not pure single component species but rather a wide distribution of homologous compounds, let us compare the actual distributions of the different surfactants and mixtures. In Figure 3, we plot the mole fraction of each EO component in each surfactant vs the HLB number of that particular fraction. These size distributions arise from the method of synthesis of the surfactant; as ethylene oxide is polymerized to nonylphenol by anionic polymerization, the resulting EO distribution is ideally a Poisson distribution. Thus, for a surfactant with an EO number of N, the relative mole fraction $x$ of any EO number component can be calculated by

\[
P(x) = N^xe^{-N}/x!
\]

For all of these components of EO = x, the HLB of the \cite{10}Griffin, W. C. J. Soc. Cosmet. Chem. 1949, 1, 311–326.

component can be calculated for nonylphenyl ethoxylates using

$$\text{HLB}(\text{EO} = x) = 20 \left( 17 + 44x \right) / \left( 220 + 44x \right)$$ (2)

where we include the terminal hydroxyl group (MW = 17) in addition to the ethylene oxide residues (MW = 44) into the hydrophilic domain.

**Case 1.** For the first case, Figure 3 shows the distribution of components for the best single surfactant, C₉PhE₆, along with the two components of the mixture, C₉PhE₄ and C₉PhE₇.5. The curves represent the actual HLB values of the components within each of the surfactants or surfactant mixtures, with the distribution of components calculated from eq 1 and the HLB values for each EO component from eq 2. From Figure 3 it can be seen that C₉PhE₆ has the bulk of its material in the HLB 9–13 region, which can be expected for good water-in-oil microemulsion solubilization. For the mixtures, the peak solubilization case (a 50:50 mixture of C₉PhE₄ and C₉PhE₇.5, with an HLBₘᵄₓ = 10.5) is plotted. This EO distribution of the mixture has a shape similar to the distribution curve for the best single surfactant (C₉PhE₆), although somewhat wider. Again, it appears that the best solubilization for the mixture occurs where the mixture

**Figure 3.** Distribution of components in single nonylphenyl ethoxylate surfactants, as well as mixtures, for case 1.

**Figure 4.** Distribution of components in single nonylphenyl ethoxylate surfactants, as well as mixtures, for case 2, showing evidence for synergism.
has most of its components in the HLB 9–13 region. This supports the concept that good solubilization occurs when most of the surfactant falls in a certain HLB region, being neither very water soluble nor very oil soluble. This should cause conditions where it is most favorable for the surfactant to partition at the interface. In such a case, solubilization for the mixtures is better than that of either component. The best mixture does not solubilize more than the best single surfactant, C₉PhE₆, with a similar EO number distribution (Figure 2). Thus, the solubilization ability in this case appears to be related only to simple additive contributions of the surfactant material in the HLB 9–13 region, with no apparent additional benefit from synergism between the two surfactants.

Case 2. Figure 4 shows a second, much different scenario. The two components in this mixture, C₉PhE₁.₅ and C₉PhE₁₂, are very oil soluble and very water soluble, respectively. Both surfactants have little of their material in the HLB 9–13 region. The plot of the distribution for the optimum mixture (43 wt % C₉PhE₁₂, HLB mix = 9) does not have a single maximum. Given the composition of individual components, the optimum mixture actually has a minimum of material in the HLB 9–13 region. In this case, the high level of solubilization has nothing to do with the amount of this material, which is completely opposite to the previous case in Figure 3. Given the conclusions of the first case, one would expect less surfactant to partition to the interface, as the two surfactant components are highly soluble in the oil (C₉-PhE₁.₅) or the water (C₉PhE₁₂) phases. This must not be the case, though, as mixtures of these two surfactants clearly show the highest water solubilization, even greater than the best single surfactant (C₉PhE₆). Some true synergistic effect must cause these components to preferentially partition to the interface, for only if the majority of surfactant partitions to the interface can such a high level of solubilization be achieved.

Conclusions

Two different approaches for surfactant selection can be considered in order to achieve a high level of water solubilization in water-in-oil microemulsion formulations. The first approach is to maximize the amount of surfactant in the HLB 9–13 region, where it is intermediate between high oil solubility and high water solubility. Achieving more surfactant partitioning to the interface as opposed to partitioning into the bulk phases will allow for stabilization of a larger interfacial area and thus a high level of solubilization. Even greater solubilization can result if some synergism between surfactant components can be achieved. As a second approach, mixtures of a highly oil soluble surfactant and a highly water soluble surfactant achieved the maximum water solubilization, evidently overcoming the expected partitioning of the two surfactant components into the oil and water phases and enhancing their partitioning to the interface.

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