Chapter 10

196– 205 (1996)

Enhanced Solubilization in Water-in-Oil Microemulsions Using Mixtures of Nonionic Surfactants

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A microemulsion can be defined as a thermodynamically stable, transparent dispersion of two immiscible liquids, stabilized by an interfacial film of surfactants. Microemulsions have many applications in such diverse areas as pharmaceutical preparations and enhanced oil recovery (1–4). Nonionic surfactants are more suitable than ionic surfactants for use in the food and pharmaceutical industries, because they are generally less toxic, produce less skin irritation, and many are classified as "generally recognized as safe" (GRAS). Another advantage of microemulsions made from mixtures of nonionic surfactants is that they are cosurfactant free. A typical microemulsion may be created with an anionic surfactant and a short-chain alcohol, such as butanol or pentanol (5). Potential applications exist in the food and pharmaceutical areas where it is not acceptable to include such ionic surfactants or alcohols, neither of which can be consumed.

The microemulsion design process involves the proper selection of surfactants and cosurfactants for given aqueous and oil phases. It is desirable to achieve the required solubilization with a minimum amount of surfactant. Much work has been done to characterize water-in-oil microemulsions for a wide variety of aqueous solutions, oils, surfactants and cosurfactants (6–11). For *macro*emulsions, concepts such as Griffin's hydrophile-lipophile balance (HLB) have proven useful in the selection of the appropriate ratio of surfactants necessary to achieve maximum solubilization (12,13). We investigate the value of the HLB idea in the design of microemulsions.

In the current paper, we concentrate on water-in-hexadecane microemulsions made with mixtures of sorbitan esters (Span) and ethoxylated sorbitan esters (Tween), as well as water-in-cyclohexane microemulsions made with mixtures of nonylphenyl ethoxylates (Igepal CO). In many cases, a high level of solubilization can be achieved by the selection of the appropriate ratio of surfactants. Often, each surfactant individually will be quite poor in aiding the solubilization of water. However, synergism exists in certain mixtures, allowing solubilization far in excess of the capability of the individual surfactants. This synergism does not occur in all cases, and some examples of a lack of synergism will be presented.

The Span and Tween families of surfactants were chosen because they offer a variety of hydrophobic and hydrophilic structures, and cover a wide range of HLB values. The Igepal CO series offers a large number of hydrophilic domain lengths, with a corresponding wide range of HLBs. Other Igepal classes provide different hydrophobic structures. This variety provides a good opportunity for surfactant structure studies.

Materials and Methods

The sorbitan ester surfactants (Span and Tween series) were donated by ICI Americas, Inc. (Wilmington, DE). The nonylphenol ethoxylate surfactants (Igepal CO series) were donated by Rhone-Poulenc, Inc. (Cranbury, NJ). All surfactants were used as received. One must be aware that these commercial surfactants are not monomerically pure. There is a considerable distribution in both the hydrophilic and hydrophobic structures of the surfactant molecules. For the hydrophilic domain, the quoted number of ethylene oxide (EO) residues is a number average of EO residues per surfactant molecule. There will be a Poisson distribution of molecules containing different EO numbers. This distribution approaches a Gaussian distribution for sufficiently large EO numbers. For the sorbitan ester surfactants, there is also variation in the sorbitan structure. The sorbitan ring is created by a dehydration of sorbitol to form 1,4-sorbitan (14). This reaction is not run to completion, thus there is residual sorbitol remaining. Also, there are some unwanted second dehydrations which result in the dual ring 1,4-3,6-isosorbide structure. In the hydrophobic domain, there is some variation due to the purity of the dodecanoic acid and oleic acid that are bonded to the sorbitan through an ester linkage. The dodecanoic acid will contain measurable amounts of decanoic acid and tetradecanoic acid, whereas the oleic acid will contain stearic, palmitic and linoleic acids.

Table 10.1 lists the sorbitan ester, ethoxylated sorbitan ester, and nonylphenol ethoxylate surfactants used. Hexadecane (99%) and cyclohexane (99%) were purchased from Fisher Scientific (Fairlawn, NJ). Water was deionized and distilled.

TABLE 10.1
Surfactants Used in This Investigation

Trade name	Structure	EO #	HLB
Span 20	Sorbitan monolaurate	0	8.6
Span 80	Sorbitan monooleate	0	4.3
Span 85	Sorbitan trioleate	0	1.8
Arlacel 83	Sorbitan sesquioleate	0	3.7
Tween 81	POE 5 sorbitan monooleate	5	10
Tween 85	POE 20 sorbitan trioleate	20	11
Igepal CO-210	Nonylphenyl ethoxylate	1.5	4.6
Igepal CO-430	Nonylphenyl ethoxylate	4	8.8
Igepal CO-530	Nonylphenyl ethoxylate	6	10.8
Igepal CO-610	Nonylphenyl ethoxylate	7.5	12.2
Igepal CO-720	Nonylphenyl ethoxylate	12	14.2

Solubilization experiments were performed by a dropwise titration of water into the oil/surfactant mixture. The mixture is constantly stirred, and a transition from cloudy to clear solution is observed for the solubilization of water. As the point of maximum solubilization is approached, the time for water solubilization becomes increasingly longer. The maximum was determined either by the lack of a transition to clear solution after several hours of stirring, or by a noticeable increase in viscosity due to the onset of liquid crystal formation. Liquid crystal formation is confirmed by the use of crossed polarizing plates, placed on each side of the sample vial. If a liquid crystalline phase is present, light will pass through the plates, due to the birefringence of the liquid crystal. Quasi-elastic light scattering measurements were performed using a Brookhaven Instruments (Holtsville, NY) BI-2030 Digital Correlator and an argon ion laser. All experiments were performed at 25°C.

The following proportions were used for the microemulsion systems. Because the variable in these cases was the amount of water added, the surfactant to oil ratio was kept fixed. For the Span/Tween mixtures, the initial surfactant/hexadecane ratio was 0.36 by weight. For the Igepal mixtures, the initial surfactant/cyclohexane ratio was 0.20.

Discussion

Long ago, it was suggested that the HLB concept could be used as a design tool for emulsions (12,13,15). It was stated that a given oil had a particular "optimum HLB" associated with it, and that two surfactants could be blended in appropriate proportions so that the HLB of the surfactant mixture would be the optimum HLB. Given this optimum HLB, new surfactant combinations could be tested, with a minimum search required for the optimum ratio of surfactants, because the optimum HLB could be used as a good first estimate. For water-in-oil emulsions, this optimum HLB is usually in the 3 to 6 range. It is recommended that the two surfactants have the same hydrophobic structure, but vary in their hydrophilic structure, so that one surfactant is much more hydrophilic overall than the other. An example of such a blend would be Span 80/Tween 80, where the Span is a sorbitan monooleate, and the Tween is a polyoxyethyleneated sorbitan monooleate. The Span is much more hydrophobic than the Tween, with the Span being soluble in oil, but not water, whereas the Tween is soluble in water. In the current paper, we test whether these concepts can be applied to a selection of surfactants and mixture ratios for the design of microemulsions.

Span/Tween Mixture Results

For water-in-oil microemulsions using Span and Tween surfactants in hexadecane, the most success was found with Tween 85 as the more hydrophilic surfactant. A number of Spans were mixed with Tween 85 at various ratios to achieve different

HLB values for the mixture. Equation (1) is used to calculate the HLB of the mixture, where w_i is the weight fraction and HLB_i is the HLB of surfactant i.

$$HLB_{mix} = w_1 HLB_1 + w_2 HLB_2 \qquad (1)$$

The resulting solubilization capacities for Span 20, 80 and 85 with Tween 85 can be seen in Fig. 10.1. Several aspects of this figure are noteworthy. First, the optimum HLB for these surfactant mixtures occurs at an HLB in the range of 8 to 11, much higher than that expected for emulsions. Second, not all of the Span surfactants show enhanced solubilization when mixed with Tween 85. The most hydrophobic surfactant, Span 85, apparently has no contributing effect at all. Third, the peak in solubilization is not symmetric. It appears that solubilization rises exponentially with increasing HLB up to a critical point, where it drops off sharply. Finally, the optimum HLB has quite a large variation, with the optimum at an HLB of 9 for Span 80/Tween 85 and 10.4 for Span 20/Tween 85. Such a wide variation is not expected for such similar surfactants.

The apparently large variation in the optimum HLB can be explained when the ratios of the surfactants are taken into account. In Fig. 10.2, the data from Fig. 10.1 is replotted using the weight percent of Tween 85 in the mixture rather than the HLB as the abscissa. From this plot, it appears that the optimum solubilization

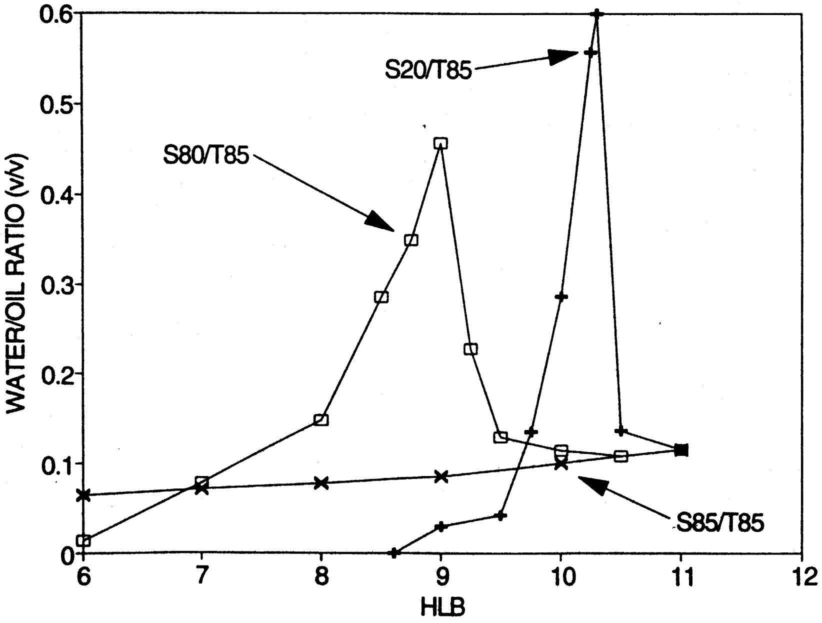

Fig. 10.1. Maximum water solubilization *vs.* HLB for binary mixtures of Span (20,80,85) and Tween 85. The surfactant to oil ratio is 0.36.

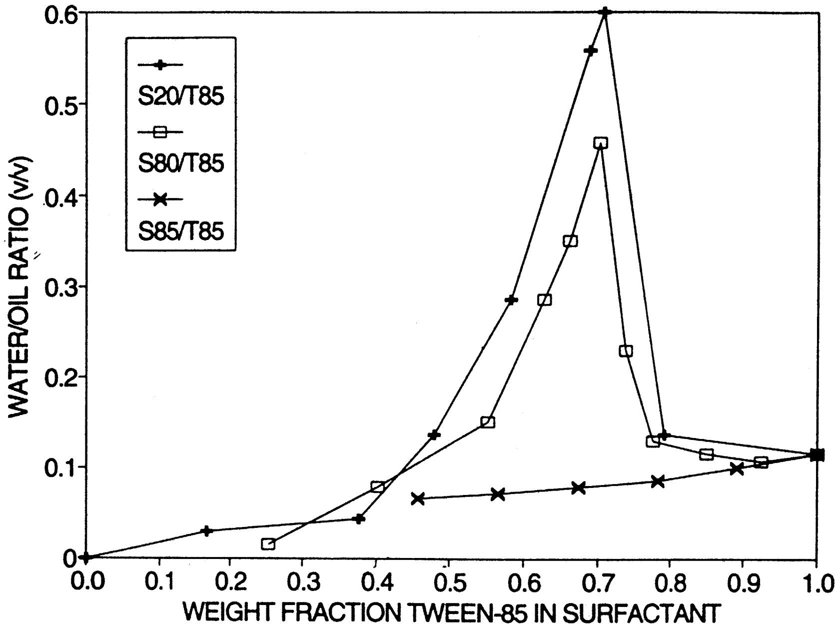

Fig. 10.2. Maximum water solubilization *vs.* weight fraction Tween 85 for binary mixtures of Span (20,80,85) and Tween 85.

occurs at a particular ratio of Span/Tween of approximately 0.7, rather than at a particular HLB. This is an interesting result, suggesting that it is the packing ratio at the interface, rather than the specific hydrophobicity of the Span (with the exception of Span 85, to be discussed later), that controls the microemulsion solubilization capacity.

Some more complicated ternary mixtures of surfactants were attempted, to determine whether the addition of a third surfactant would improve the solubilization results (see Fig. 10.3). Arlacel 83 can be thought of as a blend of two Spans, because it is a mixture of sorbitan mono- and dioleates. The second ternary system contains a fixed proportion of 1:1 for the mixture of Span 20 and Span 80. The Arlacel 83/Tween 85 system shows the highest water solubilization achieved to date with these Span/Tween systems, with a water/oil ratio of 0.78. These ternary systems show the features noted earlier: an optimum HLB in the 8 to 11 range, and an exponential increase in solubilization with increasing HLB, followed by a sharp dropoff after a critical point.

A calculation of the molar ratio of water solubilized to surfactant can give an estimate of whether the solubilized water exists in droplet form. Figure 10.4 shows a comparison of Span/Tween solubilization results with a hydration calculation, in which it is assumed that one molecule of water is bound to or associated with each oxygen of the hydrophilic domain of the surfactant molecule. For the given amount

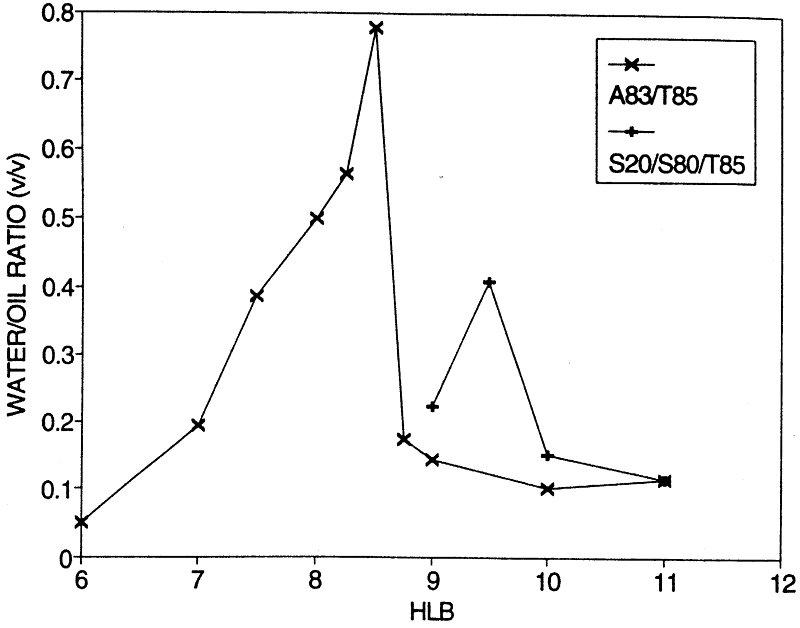

Fig. 10.3. Maximum solubilization *vs.* HLB for ternary mixtures of Spans and Tween 85.

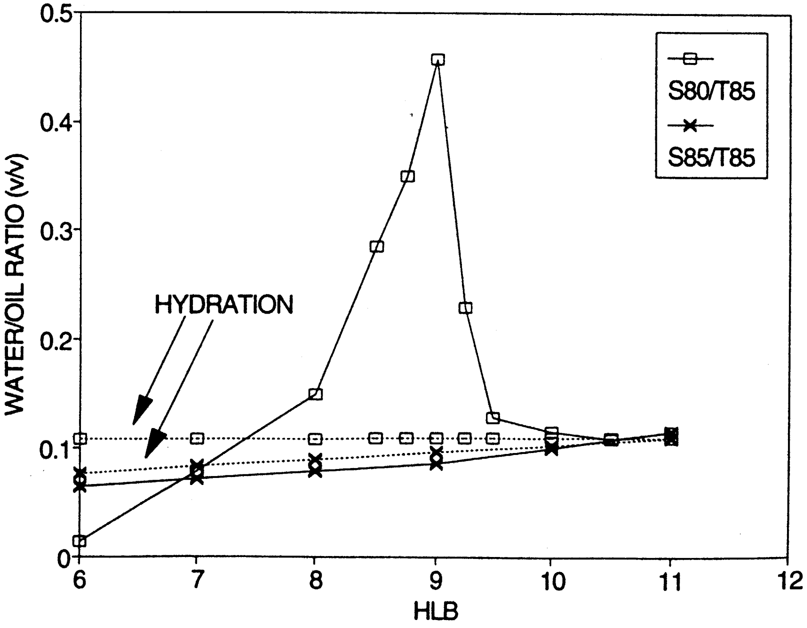

Fig. 10.4. Expected solubilization from surfactant hydration (dashed line) compared with maximum solubilization (solid line).

of surfactant present, this solubilization due to hydration is estimated to be in the 0.05 to 0.1 range for the water/oil ratio. There are several interesting aspects of the graphs in Fig. 10.4. First, the solubilization capacity of the surfactant to the right of the critical point of maximum solubilization drops down to this calculated hydration level. Second, the mixture that showed no synergism, the Span 85/Tween 85 case, solubilizes water only at this surfactant hydration level. Third, for surfactant mixtures of low enough HLB (<7), not even this hydration level of water solubilization can be reached. To test for the existence of droplets, samples of Span 80/Tween 85 and Span 85/Tween 85 at HLB values of 8.5 and 10 were analyzed using quasi-elastic light scattering. The absence of scattering for both HLB 10 cases confirmed that no microemulsion droplets exist to the right of the solubilization peak. For HLB 8.5, the Span 80/Tween 85 mixture had a strong scattering signal, whereas the Span 85/Tween 85 mixture had none, evidence that in the region of enhanced solubilization by these mixtures, microemulsion droplet formation has occurred.

It is interesting to note that synergism does not occur in all mixtures with the expected optimum HLB value or optimum molecular ratio of surfactants. The Span 85/Tween 85 pair is clear evidence of this. For this combination, it is likely that Span 85 is so hydrophobic that it is no longer surface active. It may exist solely in the oil phase, with no surface excess concentration that one would expect of a surfactant. The solubilization of water by this mixture as seen in Fig. 10.2 gives the impression that the solubilization is due only to the hydration of the Tween 85, which falls with decreasing weight fraction of Tween 85 in the mixture.

There is a second case of interest in which no synergism is observed. Figure 10.5 shows solubilization results for Tween 81 mixtures. Tween 81 has an HLB of 10, which falls in the optimum HLB range; it is not surprising, then, to find that Tween 81 has a high solubilization capacity alone, of approximately 0.45 water/oil. What is surprising, however, is that mixtures of Tween 81 with various other Spans and Tweens show absolutely no synergism whatsoever. The surfactants tested cover a wide range of HLB values, both above and below that of Tween 81. Not only is solubilization less for these mixtures, but it is even less than that expected for the reduced amount of Tween 81 in the mixture. Thus, these mixtures actually have a negative synergistic effect!

Igepal Mixture Results

For the Igepal CO surfactants (nonylphenyl ethoxylates), improved solubilization using mixtures of surfactants can also be demonstrated. These surfactants are available with a wide variety of ethylene oxide polymer lengths, with a resulting wide range of HLB values. The nonylphenyl ethoxylates showed poor solubilization results in hexadecane; consequently, all studies with this surfactant class were done with cyclohexane as the oil phase. Results for the Igepal mixtures can be seen in Fig. 10.6. The most notable difference between these and the Span/Tween mixtures is that the solubilization profile seems to be symmetric around the maximum.

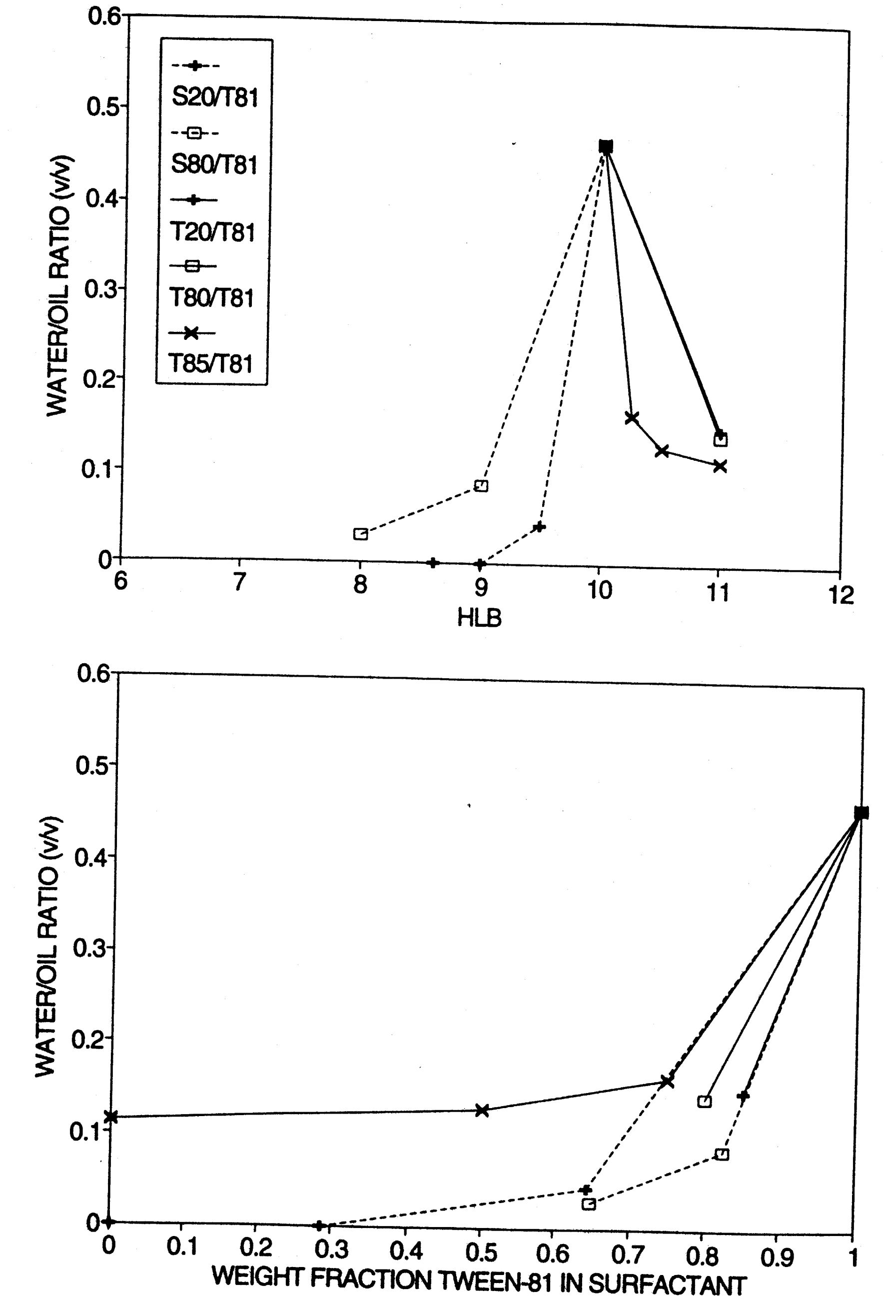

Fig. 10.5. Maximum solubilization for binary surfactant mixtures with Tween 81 *vs.* HLB (10.5a) and weight fraction Tween 81 (10.5b).

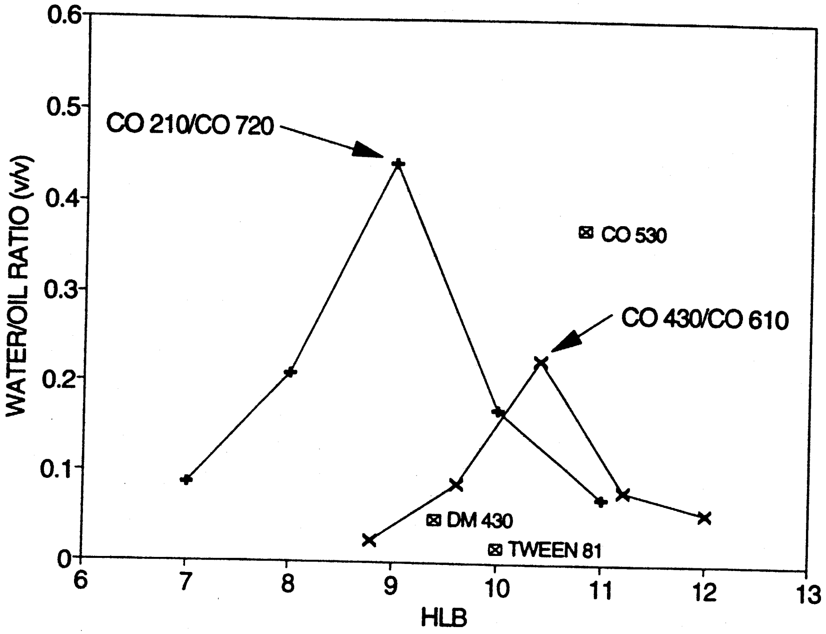

Fig. 10.6. Maximum solubilization *vs.* HLB for Igepal mixtures. The surfactant to oil ratio is 0.20.

The synergistic effect is quite obvious for these Igepal mixtures. Igepal CO-430 has an HLB of 8.8 and a relatively low solubilization capacity of water in cyclohexane. Mixtures of CO-210 and CO-720, though, have much greater solubilization capacity at the apparent optimum HLB of 9. Other single surfactants with HLB values in the optimum range, Igepal DM-430 and Tween 81, also do not have much solubilization capacity. The exception is Igepal CO-530, which has better solubilization capacity than the CO-430/CO-610 mixture. As with the Span/Tween mixtures in hexadecane, these Igepal mixtures all show maximum solubilization in the HLB 8 to 11 range.

Conclusions

From the above experiments, the following can be concluded:

1. Mixtures of surfactants generally lead to superior solubilization results for water-in-oil microemulsions. This has been established for mixtures of sorbitan esters (Spans) and ethoxylated sorbitan esters (Tweens) in hexadecane, and mixtures of nonylphenyl ethoxylates in cyclohexane.
2. When synergism occurs, solubilization is greater than simple hydration of the surfactant molecules.

3. Mixtures do not always lead to improved solubilization. No synergism is seen for mixtures of Spans and Tweens with Tween 81. Also, no synergism is demonstrated for the Span 85/Tween 85 mixture.
4. The highest solubilization achieved for binary mixtures of Spans with Tween 85 is 0.55 water/oil ratio. The best solubilization for ternary mixtures is 0.78 water/oil.
5. Good nonionic water-in-oil microemulsions can be made without the use of cosurfactants.
6. Optimum water-in-oil microemulsions occur in the HLB range of 8 to 11.
7. The molar ratio of Span to Tween seems to be an important factor in selection of the best mixing ratio of surfactants, in addition to the optimum HLB range.

Acknowledgments

The authors would like to thank Kraft General Foods for their support of this research.

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