

## Surfactant/Cosurfactant Association and Emulsion Stability

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### ABSTRACT

The stability of emulsions with an anionic surfactant combined with dodecanol and ethylene glycol dodecyl ether, respectively, was studied. The stability of the emulsion with the nonionic compound as cosurfactant was superior. The results are discussed, with the phase diagrams of water and the cosurfactant as a basis. The phase diagram of the nonionic compound shows a lamellar liquid crystal of superior stability against high water contents.

### INTRODUCTION

It is a well known fact that a combination of an ionic surfactant, such as sodium lauryl alcohol, with a long chain alcohol, such as lauryl alcohol, has a more superior stabilizing action for emulsions than the surfactant by itself.

The reason for this enhanced stabilizing action has been discussed, and the hypothesis of complex formation between the surfactant and the alcohol has been put forward (1), and retained its popularity for a long time (2,3). The concept has been shown to be incorrect; there are no such complexes at the interface (4). Furthermore, it has been shown that in a case where complexes obviously form (5), they have no beneficial influence on emulsion stability.

It has been suggested that one factor for enhanced emulsion stability is the packing conditions at the interface (6), and that the formation of a liquid crystalline phase of the two emulsifier components when combined with water should be an indication of a preferred lamellar packing. A lamellar packing should, per se, indicate stability of a planar interface, a beneficial structure for emulsion stability.

A proof of this relationship is obviously a rather extensive endeavor; the present publication should be viewed as a part of such material. The main reason for this separate report is the fact that emulsions with superior stability were found, and hence the results were judged sufficiently interesting to merit a publication.

### EXPERIMENTAL

#### Materials

The dodecanol was Eastman Kodak, Lot no. A6A; the hexadecane was Aldrich Chemicals 99%; the diethylene glycol dodecyl ether was from Nikkol, Japan, > 98%; and the octanoic acid used for the preparation of the surfactant was Aldrich Gold Label, 99.5%+. The water was twice distilled.

#### Preparation of the Soap

The soap was prepared in the following manner. Metallic sodium was reacted with water-free ethanol to form the ethoxide. Addition of the octanoic acid led to precipitation

of the soap. The latter was recrystallized twice from ethanol and dried over Drierite.

#### Emulsion Preparation and Stability

The emulsions were prepared by mixing for 10 sec in a Genie Vibromixer. Their size distribution was determined using a Coulter Counter, Model TA, in the following manner. 0.2 mL of the freshly prepared emulsion was diluted with 125 mL Isoton II. This solution was mixed 10 sec by the Coulter Counter stirrer and the particle size distribution determined after a further 5 sec. This was repeated 5 times and an average was recorded. The emulsion droplets were large and a 200  $\mu\text{m}$  capillary could be used. The emulsion stability was estimated from the sedimentation rates; the size of the emulsion droplets made this method convenient. The relative height of the turbid layer was measured vs time.

### RESULTS

One important factor in the description of research results of emulsion stability is the question of reproducibility. Figure 1 shows the results of four different determinations of one sample. It contained 1% sodium caprylate and 1% ethylene glycol dodecyl ether. The four lines illustrate the degree of reproducibility that can be expected. As will be observed in the following, it is adequate to distinguish between the two groups of emulsifiers.

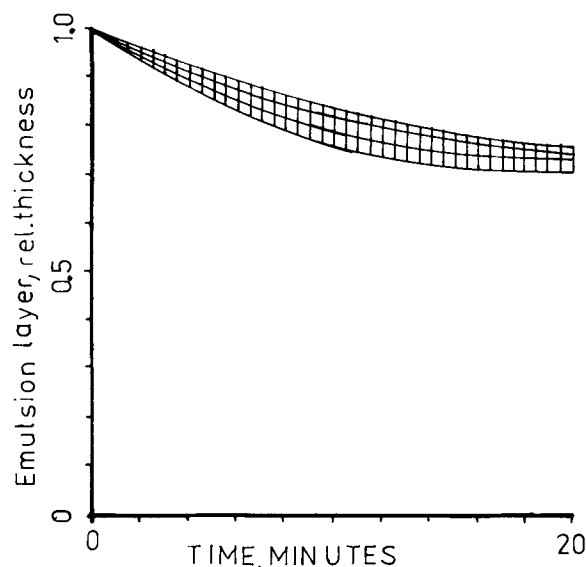


FIG. 1. The reproducibility of creaming rates is illustrated by four runs with one emulsion.

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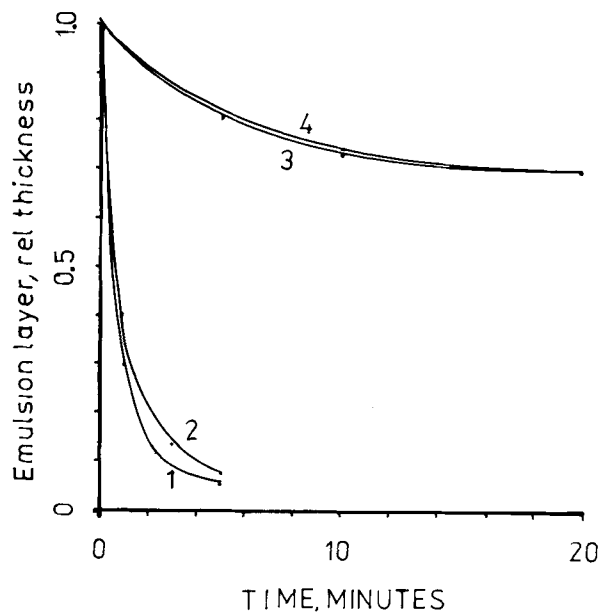


FIG. 2. Relative heights of the emulsion layer vs time.

Marking	Emulsifier, wt %		
	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
1	0.33	0.67	
2	0.5	0.5	
3	0.33		0.67
4	0.5		0.5

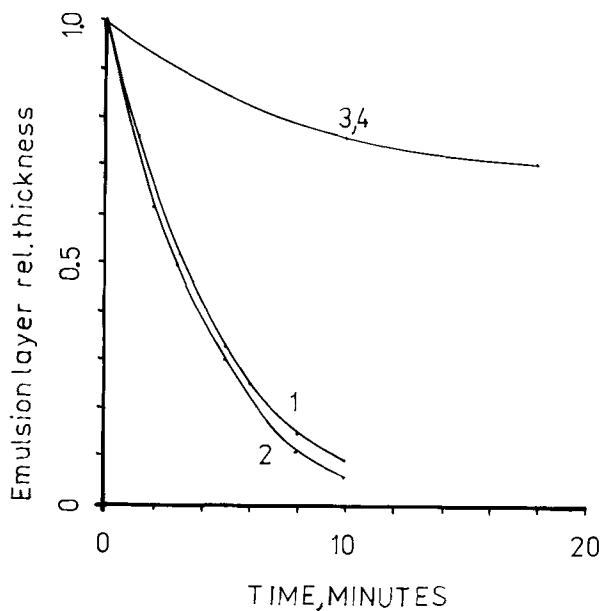


FIG. 3. Relative heights of the emulsion layer vs time.

Marking	Emulsifier, wt %		
	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
1	0.67	1.33	
2	1.0	1.0	
3	0.67		1.33
4	1.0		1.0

The results of the emulsion stability determinations are shown in Figures 2 and 3. Figure 2 shows the rate of phase separation for samples with a total of 1% emulsifier. The emulsions with the alcohol combination separated consider-

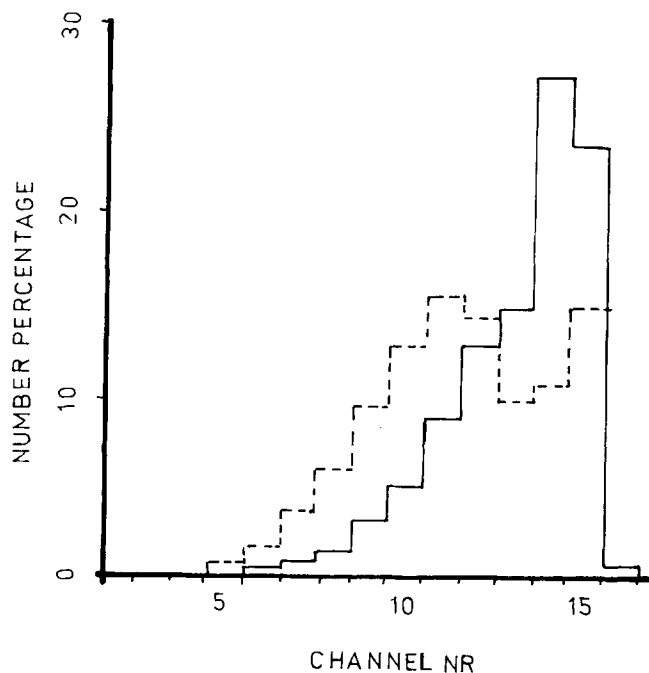


FIG. 4. Size distribution of emulsions with a total emulsifier amount of 1% by wt.

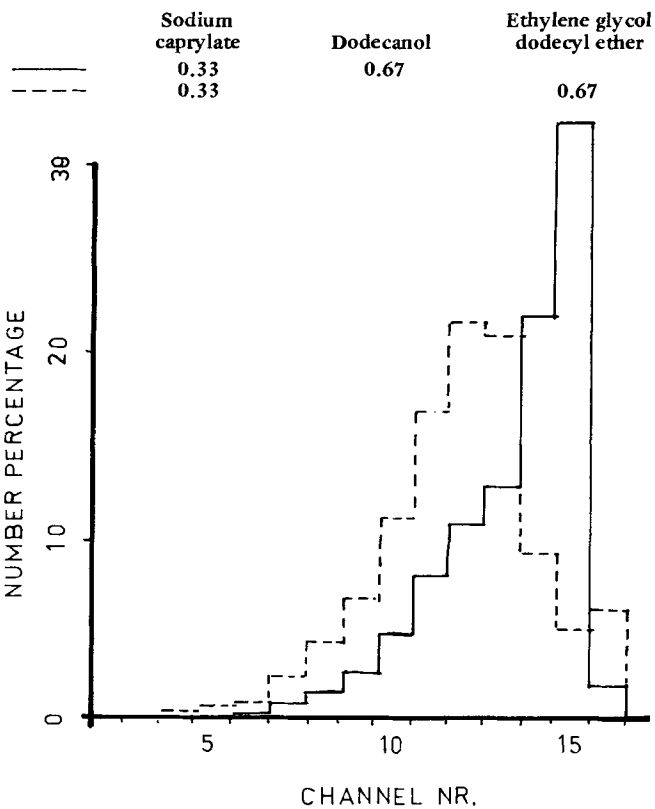


FIG. 5. Size distribution of emulsions with a total emulsifier amount of 1% by wt.

Line Style	Emulsifier, wt %		
	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
—	0.5	0.5	
- - -	0.5		0.5

ably faster than the ones stabilized with the nonionic/anionic surfactants. The different cosurfactant/surfactant ratios did not differ from each other in a significant manner. With a total of 2% emulsifier combination (Fig. 3), the

EMULSIFIER COMBINATIONS

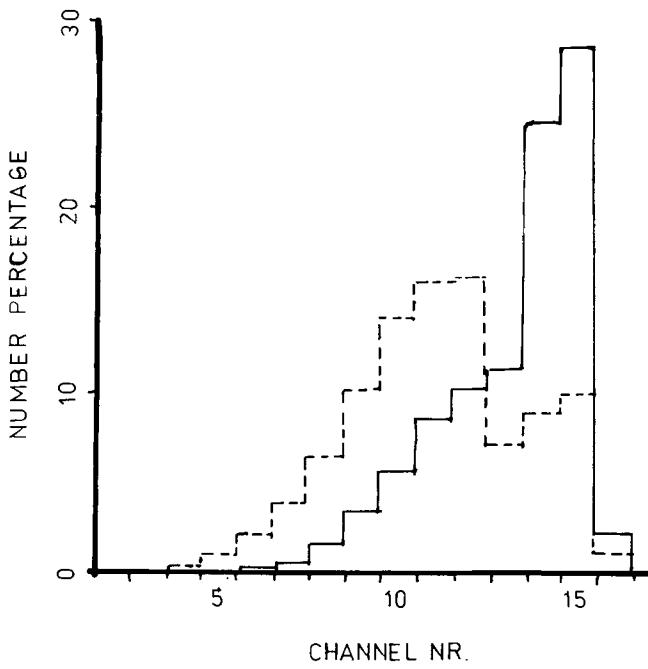


FIG. 6. Size distribution of emulsions with a total emulsifier amount of 2% by wt.

	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
—	0.67	1.33	1.33
- - -	0.67		

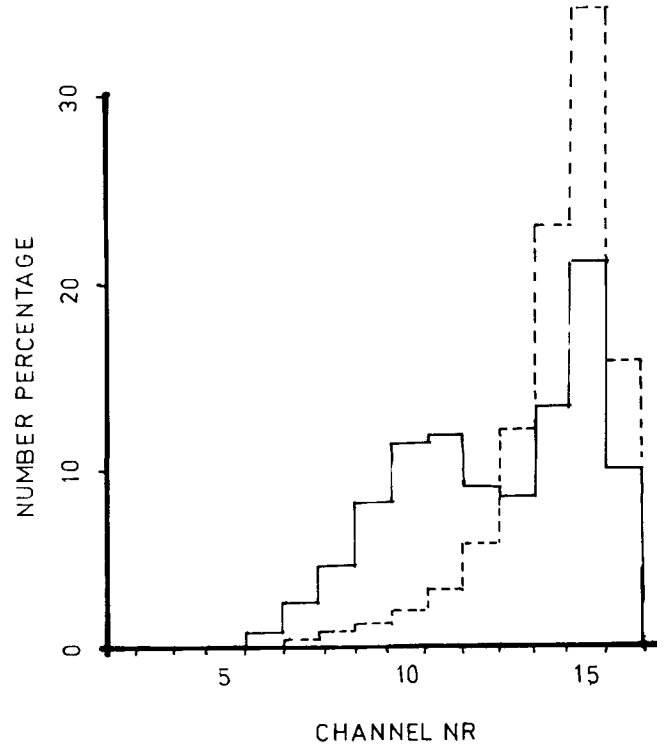


FIG. 8. Size distribution of emulsions with a total emulsifier amount of 1% by wt.

	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
—	0.5	0.5	0.5
- - -	0.5		

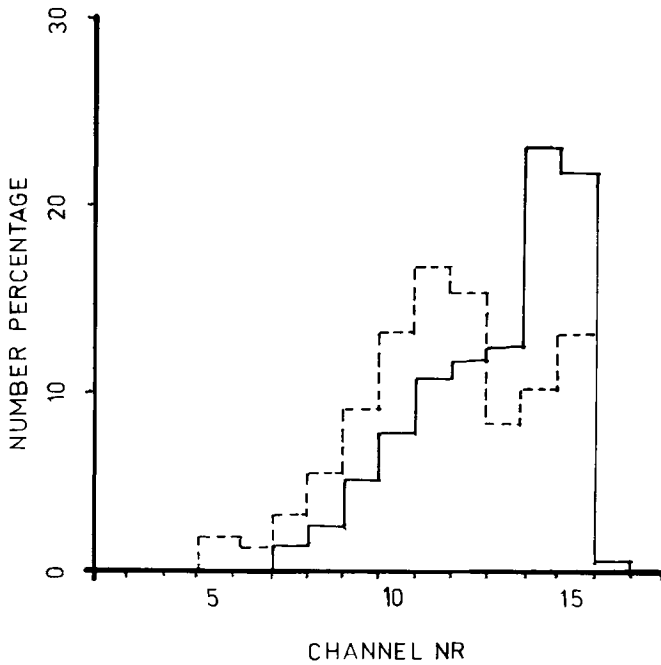


FIG. 7. Size distribution of emulsions with a total emulsifier amount of 2% by wt.

	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
—	1.0	1.0	1.0
- - -	1.0		

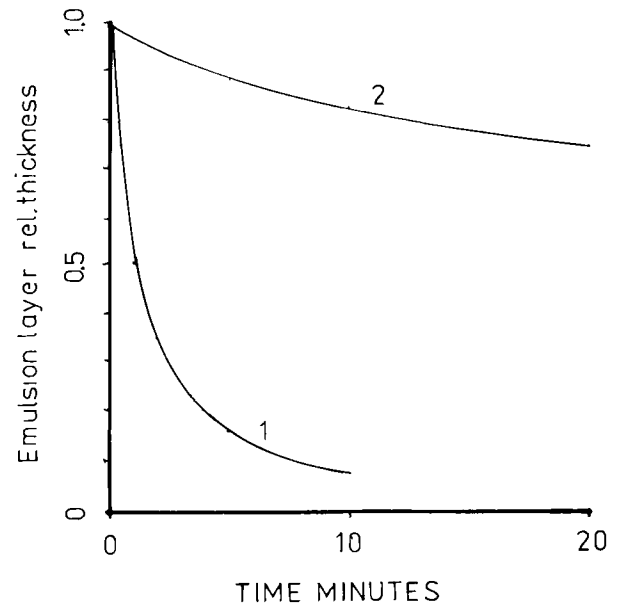


FIG. 9. Relative heights of the emulsion layer vs time.

Marking	Emulsifier, wt %		
	Sodium caprylate	Dodecanol	Ethylene glycol dodecyl ether
1	0.5	0.5	
2	0.5		0.5

stability of the alcohol combination emulsions had improved significantly. The stability of the nonionic/anionic emulsions remained identical.

The drop size distribution is an important factor for the

stability of an emulsion. At first, if smaller sizes are found for one emulsifier compared to another, the emulsification may have been made more efficient. Also, the sedimenta-

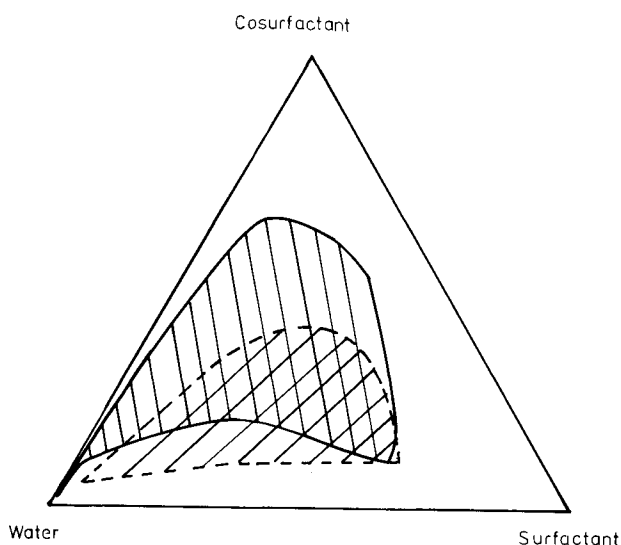


FIG. 10. The lamellar liquid crystalline phase region in a system water, surfactant (sodium dodecyl sulphate) and cosurfactant.



tion rates will be smaller for smaller sizes, which in turn will induce coalescence by the sedimentation (7).

The size distribution determined immediately after emulsification (Figs. 4-7) showed the average droplet size to be smaller for the emulsions with nonionic/anionic combinations of surfactants. To show that the changed emulsion stability was not a question of size only, the emulsion with the alcohol combination in Figure 5 was emulsified for a longer time to reach a size distribution similar to the one from the other emulsion. The soap/alcohol system now showed a distribution more toward smaller sizes (Fig. 8). In spite of this fact, the stability ratio between the two emulsions (Fig. 9) gave no significant difference from the earlier ones (compare Figs. 9 and 2).

## DISCUSSION

The improvement in the stabilization with ethylene glycol dodecyl ether as cosurfactant was pronounced. The initial rate of separation of the emulsions with an alcohol combination was 10-30 times faster than for the emulsions with the nonionic cosurfactant, and the final emulsion volume varied by a factor of ten.

A complete explanation of the results can be reached first after complementary studies in which adsorption isotherms are determined, as well as interfacial tensions. Awaiting these results, we would for the time being relate these preliminary results to some studies on association structures in a similar system.

These results are concerned with the change of phase regions in systems of water and combination surfactants and will be published elsewhere (8). Of interest for the present investigation is the modification of the phase diagram when a long chain alcohol is replaced by a hydrophobic nonionic surfactant. Figure 10 reveals the region of the lamellar liquid crystalline phase for the system water, sodium dodecyl sulphate with decanol, or diethylene glycol dodecyl ether as the third component. The nonionic surfactant as the cosurfactant gives a larger area for the lamellar liquid crystalline phase. The region reaches toward more high cosurfactant/surfactant ratios than the alcohol liquid crystal does. The limiting cosurfactant/surfactant ratio was 17 for the phase with the nonionic cosurfactant; the corresponding value for the structure with the alcohol was only 2. In addition, the liquid crystalline phase with the nonionic cosurfactant tolerates higher water concentrations. 98% water is found in its structure; with the alcohol as cosurfactant the maximum water content was 90%.

These variations should be related to recent results by Rydhag et al. (9). They found the stabilizing action of a liquid crystalline phase containing lecithin to be dependent on the presence of an ionic surfactant. Such a presence conveys a charge to the interface, adding to the stability by the conventional electric double layer compression, but also gives lamellar liquid crystals with a considerably higher capacity for solubilizing water (10). It is interesting to note the high water solubilization capacity of the lamellar liquid crystal with the nonionic emulsifier in the present investigation.

Speculations about actual contents of liquid crystals in the emulsions are tempting, but without meaning before more experimental evidence has been collected.

## ACKNOWLEDGMENT

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