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01 Jan 1986

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### Recommended Citation

R. L. Venable et al., "Microemulsions With High Water Solubilizing Capacity At High Hydrocarbon Levels And Very Low Surfactant Concentrations," *Journal of Colloid And Interface Science*, vol. 109, no. 2, pp. 330 - 335, Elsevier, Jan 1986.

The definitive version is available at [https://doi.org/10.1016/0021-9797\(86\)90311-5](https://doi.org/10.1016/0021-9797(86)90311-5)

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# Microemulsions with High Water Solubilizing Capacity at High Hydrocarbon Levels and Very Low Surfactant Concentrations

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Received February 18, 1985; accepted June 4, 1985

Phase diagrams have been determined showing the extent of the inverse micellar or microemulsion region for systems consisting of water-surfactant-cosurfactant or water-surfactant-hydrocarbon cosurfactant mixture with three surfactants and four cosurfactants. The surfactants are sodium dodecyl sulfate, sodium laurate, and tetradecyltrimethylammonium bromide while the cosurfactants are pentanol, hexanol, pentylamine, and hexylamine. Hexylamine is found to be a very effective cosurfactant giving rise to very good water solubilizing capacity at extremely low surfactant concentrations and very low cosurfactant levels at rather high initial hydrocarbon levels. © 1986 Academic Press, Inc.

## INTRODUCTION

Microemulsions have been studied extensively since their introduction by Hoar and Schulman (1). Some fairly extensive reviews and/or overviews are available (2-4) which give the historical background and a fairly up to date presentation of the state of knowledge about microemulsions. Ionic surfactants generally require use of a cosurfactant to form microemulsions and the emphasis has been heavily on medium-chain-length alcohols (5, 6) with possibly some use of glycol type compounds or organic acids and even occasionally tertiary amines (7, 8). Microemulsions typically require 6-10% by weight of surfactant and 8-14% cosurfactant (4). Friberg and Buraczewska (9) have also observed that, as the hydrocarbon level goes above 50% of the components other than water, the ability to solubilize water decreases sharply. This limits the ability to dilute the microemulsion system with the hydrocarbon or to add large amounts of water.

Greatly enhanced water-solubilizing ability is observed at high hydrocarbon levels when quaternary ammonium salts are used in place

of the more common anionic surfactants (10, 11). These systems still require the usual amounts of surfactant and cosurfactant. However, as recently pointed out (12), use of hexylamine as cosurfactant in place of the more commonly used medium-chain-length alcohols holds promise of greatly reducing the problems associated with solubilization of water at high hydrocarbon levels. The present paper reports a study of the phase diagrams of some common surfactants using hexylamine, pentylamine, pentanol, and hexanol as cosurfactants in an effort to learn the reason for the great effectiveness of hexylamine under the conditions used in these experiments.

## MATERIALS AND METHODS

*Materials.* The sodium dodecyl sulfate (SDS) was BDH specially pure and was recrystallized twice from ethanol before use. The sodium laurate (SL), pentylamine, hexylamine, and hexanol were purchased from Sigma Chemical Company and used as received. Tetradecyltrimethylammonium bromide (TTMAB) was also purchased from Sigma but was recrystallized by dissolving in a minimal amount of methanol then adding diethyl ether until precipitation occurred. After filtration, the residual ether was removed

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from the precipitate by evacuation in a desiccator. This process was repeated until a plot of surface tension vs the logarithm of surfactant concentration showed no minimum. Pentanol and heptane were purchased from Fisher and used as received. The water was double distilled, once from an acidic permanganate solution and once just as a simple distillation from an all-glass system.

*Methods.* For the titration experiments, dry surfactant was weighed into screw-cap culture tubes, the requisite amount of cosurfactant or of hydrocarbon-cosurfactant mixture added, and then the water was added dropwise. Samples were stirred vigorously on a vortex mixer after each addition of water. The endpoint of the titration was taken to be the appearance of permanent turbidity or of optical birefringence as observed between crossed polarizers.

At the end of a titration the samples were stored for several days to be sure that the turbidity or optical birefringence was indeed permanent. As a further check on the systems with hexylamine as cosurfactant particularly, several series of samples were prepared for long-term storage. In a given series the surfactant-cosurfactant ratio was held constant and varying amounts of water added at concentrations below those which gave turbidity or optical birefringence in the titration. These were stored for the periods of time indicated in Table I in each case to see if phase separation occurred. The results of the long-term storage experiments generally agreed with the titration results within 2 or 3%. The long-term storage results are the ones presented where there was a difference. All measurements were carried out at  $23 \pm 1^\circ\text{C}$ .

TABLE I  
System Composition at Maximum Water Solubilization

Storage time	Cosurfactant	Percentage composition				
		Water	SDS	Cosurfactant	Heptane	SL
A. Water-SDS-cosurfactant						
30 days	Hexylamine	67.8	1.0	31.2	—	—
21 days	Hexanol	39.1	15.2	45.7	—	—
Titration	Pentanol	82.1	5.9	12.0	—	—
B. Water-SDS-25% heptane-75% cosurfactant						
20 days	Hexylamine	92.0	0.8	5.4	1.8	—
Titration	Hexanol	43.1	14.8	31.6	10.5	—
Titration	Pentanol	50.1	11.4	28.9	9.6	—
C. Water-SDS-50% heptane-50% cosurfactant						
30 days	Hexylamine	85.0	1.8	6.6	6.6	—
14 days	Hexanol	41.4	13.5	22.6	22.6	—
Titration	Pentanol	43.5	11.3	22.6	22.6	—
Titration	Pentylamine	74.1	5.1	10.4	10.4	—
D. Water-SDS-75% heptane-25% cosurfactant						
30 days	Hexylamine	60.0	2.8	9.3	27.9	—
Titration	Hexanol	21.2	10.2	17.1	51.4	—
Titration	Pentanol	21.1	8.7	17.6	52.7	—
Titration	Pentylamine	18.3	12.3	17.4	52.1	—
E. Water-SL-75% heptane-25% hexylamine						
30 days		85.0	—	3.6	10.7	0.7

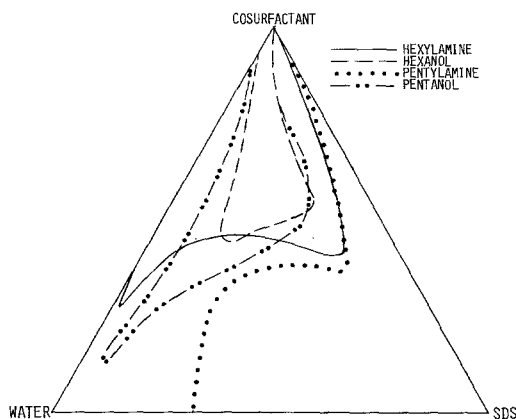


FIG. 1. Microemulsion or  $L_2$  region in the system water-SDS-cosurfactant.

### RESULTS

The microemulsion regions for the system water-SDS-cosurfactant are shown in Fig. 1 with the four cosurfactants. With hexylamine there definitely is a normal micellar region and a lamellar liquid crystalline region, but the magnitude and properties of these regions are beyond the scope of this work and will be reported in a later publication. The existence of these various regions is possible with the other cosurfactants but has not been investigated in this work. The diagrams shown in Fig. 1 lie in the base plane of a four-component diagram. Results for the systems with water-SDS-25% heptane-75% cosurfactant

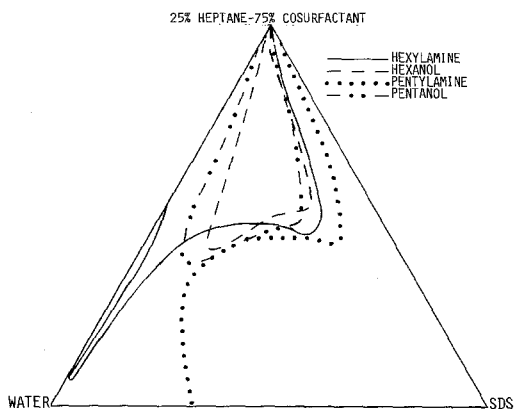


FIG. 2. Microemulsion or  $L_2$  region for the system water-SDS-25% heptane-75% cosurfactant.

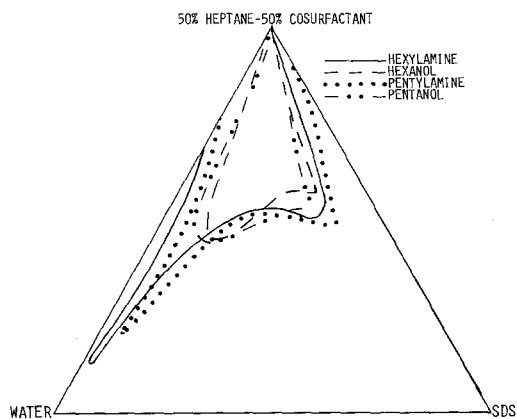


FIG. 3. Microemulsion or  $L_2$  region for the system water-SDS-50% heptane-50% cosurfactant.

are shown in Fig. 2 while those for 50% heptane-50% cosurfactant appear in Fig. 3 and those for 75% heptane-25% cosurfactant appear in Fig. 4.

The pseudoternary phase diagrams with water-SL-75% heptane-25% hexylamine as well as the same diagram with TTMAB as the surfactant are shown in Fig. 5. Figure 6 for 85% heptane-15% hexylamine shows that the ability to solubilize water still drops rather dramatically as hydrocarbon levels rise above 75% even with hexylamine as cosurfactant, particularly for SL and TTMAB. Figure 7 presents phase diagrams for TTMAB at 0, 25, and 50% heptane. The figure is a bit busy but the results at 50% heptane are shown as an

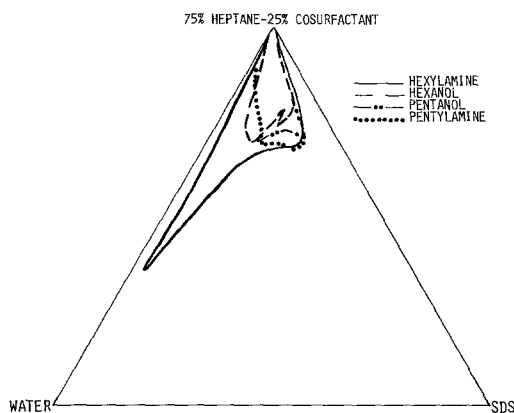


FIG. 4. Microemulsion or  $L_2$  region in the system water-SDS-75% heptane-25% cosurfactant.

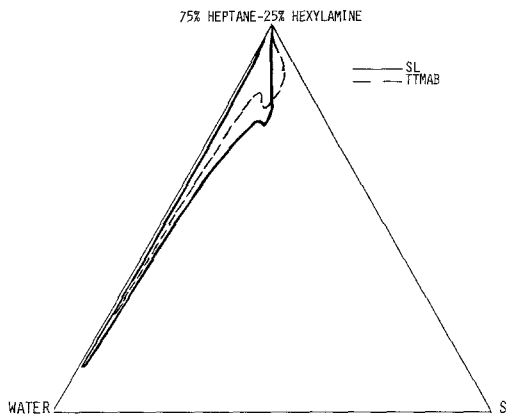


FIG. 5. Microemulsion or  $L_2$  region in the system water-surfactant-75% heptane-25% hexylamine.

inset so that the shape of the phase diagram in the region of maximum water solubilization is clearly visible.

For systems involving SDS or SL the composition of each system at the point of maximum water solubilization is given in Table I, while the results for TTMAB are given in Table II.

DISCUSSION

In the methods section mention was made of checking titration results by long term storage for certain samples as indicated in Table

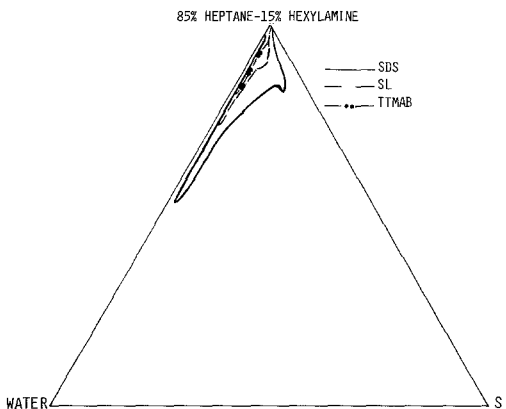


FIG. 6. Microemulsion or  $L_2$  region in the system water-surfactant-85% heptane-15% hexylamine.

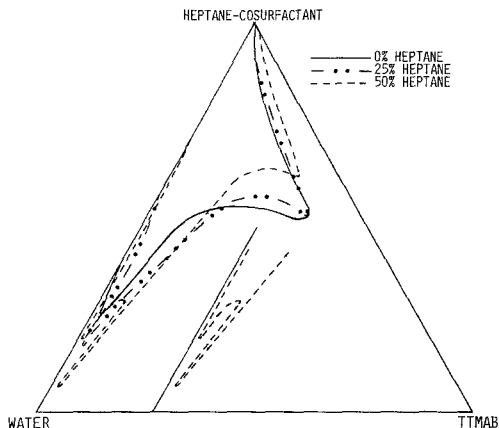


FIG. 7. Size and shape of the microemulsion or  $L_2$  region in the system water-TTMAB-heptane-hexylamine as a function of heptane level.

I. Since the solutions which first showed turbidity during a titration were kept for several days to be sure the turbidity was permanent, the water-solubilizing capacity or water solubility limit determined by long-term storage is always less than that determined by titration where there is a difference. The system with 85% heptane-15% hexylamine with SDS is the only system that showed a significant difference between the titration and long-term storage results. In that system titration gave 46% water solubilized at the maximum point, but a considerable degree of phase separation occurred almost immediately. Long-term storage gave only 32% water solubilized at the maximum point.

TABLE II

System Composition at Maximum Water Solubilization for TTMAB at the Various Hydrocarbon Levels Studied

Hydrocarbon level (%)	Percentage composition			
	Water	TTMAB	Hexylamine	Heptane
0	72.7	1.4	25.9	0
25	80.5	2.0	13.1	4.4
50 <sup>a</sup>	79.6 <sup>a</sup>	1.2 <sup>a</sup>	9.6 <sup>a</sup>	9.6 <sup>a</sup>
50	91.3	1.7	3.5	3.5
75	73.9	0.7	6.3	19.0

<sup>a</sup> Data for first tip or "maxima."

From Fig. 1 it is obvious that in the systems consisting of water-SDS-cosurfactant, pentanol, pentylamine, and hexylamine are much more effective at solubilizing water than is hexanol. The maximum water solubilization occurs at a lower surfactant concentration with hexylamine than with pentanol. The microemulsion region may connect with the normal micellar region in the pentanol diagram. Pentylamine and water are completely miscible so it is not surprising that the diagram with pentylamine gives one large solubility region connecting with the water-SDS axis at approximately 33% SDS in reasonable agreement with the literature (13). Comparison of Figs. 1 and 2 shows that there is no significant change in the size of the microemulsion region when 25% heptane is added to hexanol or to pentylamine. However, there is a significant enhancement of water-solubilizing capacity when 25% heptane is added to hexylamine and a marked reduction in water solubilization with pentanol. This enhancement in water-solubilizing capacity with hexylamine is probably caused by the destabilization of the lamellar liquid crystalline phase due to the presence of the heptane. In fact if the water solubilization maximum did not occur at such a low surfactant concentration, the microemulsion region with hexylamine might connect with the normal micellar region.

As shown in Fig. 3 the difference in the size of the microemulsion region with pentanol and with hexanol is not particularly striking at 50% initial hydrocarbon level. Pronounced differences in the associational structures of microemulsions stabilized with pentanol and with hexanol have been reported (5, 14) using other surfactants. It is not known if such differences exist with the present systems. As noted in the discussion of Fig. 1, pentanol competes very well with hexylamine in the absence of hydrocarbon, but as shown here in Fig. 3, the amines are far superior to the alcohols at solubilizing water with 50% hydrocarbon in the cosurfactant. Hexylamine is also obviously superior to pentylamine, both in terms of the maximum water solubilizing ca-

capacity and in terms of the lower surfactant concentration required.

The reduction in water-solubilizing capacity at hydrocarbon levels above 50% is apparent for all cosurfactants when the results in Fig. 4 are compared with those in Fig. 3. Again there is no really significant difference in the size of the microemulsion region with pentanol and hexanol or for that matter with pentylamine. The great superiority of hexylamine as a cosurfactant for solubilizing water is certainly still obvious. The extremely low surfactant level required is still readily apparent also.

The results shown in Fig. 5 for SL and TTMAB show that hexylamine is tremendously effective at solubilizing water at very low surfactant concentrations with these surfactants as well at the 75% initial hydrocarbon level. The decrease in water solubilizing capacity with increasing hydrocarbon level is further illustrated by comparing results for SDS from Fig. 4 with those in Fig. 6 and by comparing the results for SL and TTMAB from Figs. 5 and 6. This comparison shows the change in going from 75 to 85% hydrocarbon. SDS does not lose its effectiveness nearly as badly as do SL and TTMAB but even so the decrease in water-solubilizing capacity is still very pronounced.

The results shown in Figs. 5 and 6 do, however, point out that the tentative suggestion of the possible importance of something called complementarity of function put forth in a recent paper (12) was premature. That suggestion was based on too few measurements on too few surfactants, and does not appear at the present time to be valid.

Reference has already been made to previous work (10, 11) showing that, with pentanol as cosurfactant, the quaternary ammonium salts give much larger water solubilization at very high hydrocarbon levels than does the anionic SDS. Comparison of the results summarized in Tables I and II for hexylamine as cosurfactant shows that at 50% heptane and 75% heptane TTMAB is indeed somewhat superior to SDS at solubilizing water. The differences are not particularly striking and, as

already discussed, at 85% heptane the situation is reversed with SDS being superior to TTMB.

The effectiveness of hexylamine as a cosurfactant would appear to hold great promise for industrial formulations where amines can be tolerated. Hexylamine does have a pungent odor and all amines tend to be aggressive. These do pose limitations on the uses of hexylamine. However, if the factor or factors responsible for the effectiveness of hexylamine can be uncovered, then other compounds may possibly be found which can be equally effective but have fewer undesirable properties.

The one feature that appears to correlate so far is the solubility of water in the various compounds used as cosurfactants in this study. From Fig. 1 we see that water is sparingly soluble in pentanol (11%) or hexanol (8%) while being quite soluble (62%) in hexylamine. In contrast, as previously mentioned, water and pentylamine are completely miscible. Thus hexylamine is seen to be in an intermediate position between the two extremes as far as ability to dissolve water is concerned. Neither of the alcohols nor hexylamine is appreciably soluble in water. Hexanol is soluble to the extent of 0.6–0.7% by weight, hexylamine about 1%, and pentanol about 1.5%. Therefore sparing solubility in water may be a necessary condition for a compound to be a good cosurfactant for W/O microemulsion formation at high hydrocarbon levels, but does not seem to be a sufficient condition. These observations would appear to be in qualitative agreement with the concept of the hydrophile–lipophile balance (HLB) of surfactant systems as put forth by Shinoda *et al.* (15).

#### SUMMARY

In all surfactant systems studied so far in our laboratory, hexylamine has been found to give excellent water-solubilizing capacity at high hydrocarbon levels with extremely low surfactant concentrations and very low cosurfactant levels. In general, hexylamine has been

far superior to either pentylamine, pentanol, or hexanol in this regard. This superiority of hexylamine is observed with both the aliphatic hydrocarbon heptane and the aromatic hydrocarbon toluene (12). It has been observed with SDS, with the carboxylate salt sodium laurate, and with the quaternary ammonium salt tetradecyltrimethylammonium bromide. Of the possible factors which could be responsible for this behavior, the one that has been found to correlate to date is good solubility of water in the cosurfactant coupled with sparing solubility of the cosurfactant in water.

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