LIQUID SCINTILLATION COUNTING
RECENT APPLICATIONS AND DEVELOPMENT
VOLUME II. SAMPLE PREPARATION AND APPLICATIONS

EFFECTS OF EMULSIFIER BLENDING ON SAMPLE HOLDING CAPACITY OF SCINTILLATION COCKTAILS

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*Historically emulsifier cocktails have been prepared using a single emulsifier, such as Triton*X-100, with toluene and fluors. This paper will discuss the advantages of cocktail preparation using blended emulsifier systems. Blends of emulsifiers may be used to optimize specific performance such as sample capacity of the clear liquid region, stability of gel phases, or elimination of opaque regions.*

Liquid scintillation counting developed around the need to count radionucleotides emitting low-level alpha and beta radiation. The common constituents of a liquid scintillator are a solvent, usually an alkyl benzene, and one or more fluors. The purpose of the solvent is to absorb energy from radioactive disintegrations and transfer that energy to the fluor. The fluor converts the energy to light, which is measured by the scintillation counter.

A major drawback to this system is that alkyl benzenes do not permit the counting of aqueous samples as homogeneous preparations. Most samples of biological and environmental interest are aqueous solutions and, when placed in an alkyl benzene scintillator solution, form an immiscible layer. In such two-phase systems, neither accurate nor reproducible results of radioactive disintegrations can be obtained.

Two approaches have been used to eliminate this problem. The historic approach was to add small, polar organic molecules miscible with both water and scintillator solvents

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(Birks, 1964). This technique is limited to small volume and dilute aqueous samples.

Another approach is to add an emulsifier to the scintillator solution. This forms homogeneous suspensions or colliodal dispersions with aqueous samples. This technique has been more actively pursued in recent years. Meade and Stiglitz (Meade and Stiglitz, 1962) first introduced Triton* X-100, a nonionic surfactant, to emulsify aqueous samples in toluene. This is still a very popular formulation today. Lieberman and Moghissi (Lieberman and Moghissi, 1970) undertook evaluation of a large number of emulsifiers to determine which would produce optimum performance in a scintillator solution. The criteria they used to determine optimum performance was a type of Figure of Merit function.

The Figure of Merit is determined by multiplying the counting efficiency of a sample preparation by the percent sample load. For example, a 2.5 ml sample of tritiated water in 10 ml of scintillator-emulsifier solution is a 20% sample load (2.5 ml sample ÷ 12.5 ml total volume.) If this sample counts with 30% efficiency, then the Figure of Merit would be 600 (20% X 30%). Leiberman and Moghissi (Lieberman and Moghissi, 1970) observed that the most effective class of emulsifiers, based on a Figure of Merit function, were nonionic alkylphenol ethoxylates. In this class, Triton*N-101, a nonylphenol ethoxylate, worked best for the p-xylene solvent system.

Figures 1 and 2 are phase diagrams of sample load versus temperature for Triton X-100 in toluene and Triton N-101 in p-xylene. Three distinct regions are indicated in Figure 1. A two-phase region where the cocktails and aqueous sample form immiscible layers. In such a nonhomogeneous system reliable answers cannot be obtained. Two regions of homogeneity are observed: the clear liquid region which appears as a clear solution; and the gel region which appears as a firm emulsion of solvent, surface active agent and aqueous sample. Answers from these two regions are both reliable and reproducible. A fourth region is present in Figure 2. The region is labeled opaque gel and although it is homogeneous, light transmission from this phase is so poor as to render this region useless for scintillation counting.

An ideal cocktail would be homogeneous throughout its useful range--preferably between 0 and 50% sample load. Toward this end, a study has been undertaken to evaluate blends of nonionic emulsifiers. From the observation of

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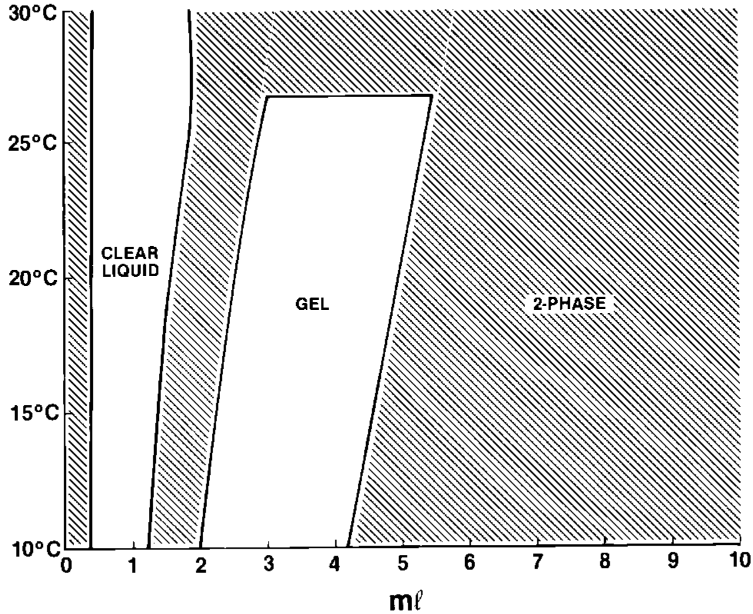

FIGURE 1. Phase diagram of ml water in 10 ml of cocktail. Formulation: 33% Triton X-100 in toluene.

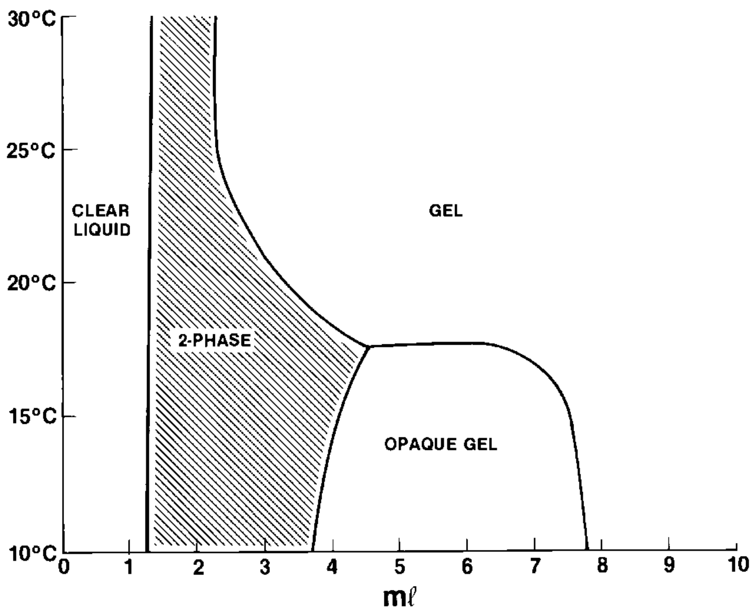

FIGURE 2. Phase diagram of ml water in 10 ml of cocktail. Formulation: 27% Triton N-101 in p-xylene. (Lieberman-Moghissi cocktail.)

Lieberman and Moghissi, (Lieberman and Moghissi, 1970) that nonylphenol ethoxylates were the most effective emulsifiers for xylene based cocktails, we limited our evaluation to nonylphenol ethoxylates. To further reduce the number of parameters tested, the solvent composition, emulsifier, and fluor concentrations were held constant. The solvent was a mixture of p-xylene and trimethylbenzene and had a flashpoint greater than 100°F. This blend is safer, less restricted by Federal regulations, and easier to handle than p-xylene. The primary fluor was PPO at 5 g/l, the secondary fluor bis-MSB at 200 mg/l. The total concentration of emulsifier was 40% by weight.

The number of different emulsifiers is in the thousands. Even restricting selection to nonylphenol ethoxylates leaves many choices. Some parameter is necessary to compare emulsifiers. Hydrophilic/Lipophilic balance (HLB number) was developed by W.C. Griffin (Griffin, 1949, 1954) in the 40's and describes emulsifying properties of a surfactant. Values vary between 0 and 20. A low HLB, such as 4, indicates an oil soluble emulsifier useful for dissolving small amounts of water into oil. A large number, such as 16, indicates a water soluble emulsifier useful for dissolving small amounts of oil into water. The HLB number can be determined experimentally or calculated for alkyl and aryl ethoxylates from Equation 1.

$$\text{HLB} = \text{weight \% ethylene oxide content} \div 5 \qquad (1)$$

Figures 3 and 4 are phase diagrams of sample capacity versus temperature for two cocktails. The cocktail represented by Figure 3 is formulated by using 40% nonylphenol ethoxylate emulsifier. This particular emulsifier has an average ethoxylate chain length of 6 moles of ethylene oxide (E.O. = 6.0). The HLB value of this emulsifier is 10.9 (HLB = 10.9). The cocktail represented by Figure 4 is formulated with 40% nonylphenol ethoxylate with an average ethoxylate chain of 12 moles of ethylene oxide (E.O. = 12.0) and an HLB value of 14.1 (HLB = 14.1). The cocktail with an ethoxylate chain of six moles ethylene oxide, Figure 3, has limited sample capacity, particularly at ambient temperatures. It has no gel region. Empirically it was determined that a cocktail formulated with a nonylphenol emulsifier having an HLB value below 10.9 would have even less sample capacity. The cocktail with an ethoxylate chain of 12 moles of ethylene oxide, Figure 4, has limited sample capacity, because of the viscous gels

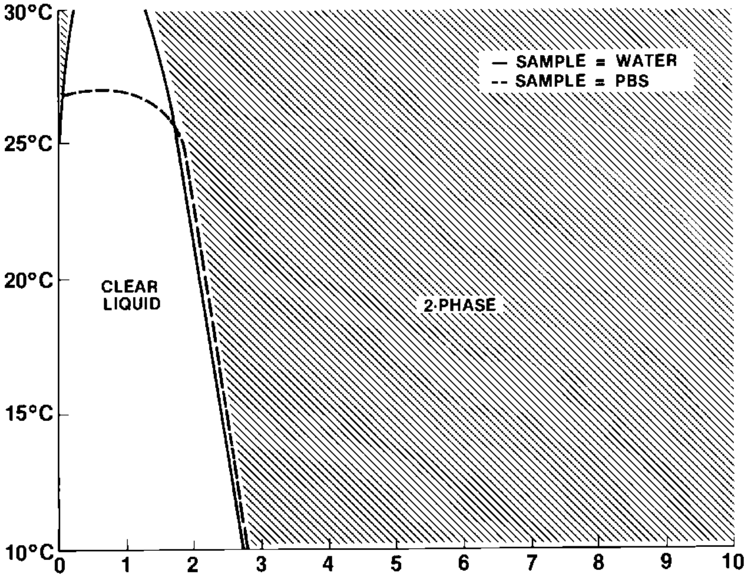

FIGURE 3. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 10.9; 40% emulsifier 1, E.O. = 6.0. PBS is phosphate buffered saline solution.

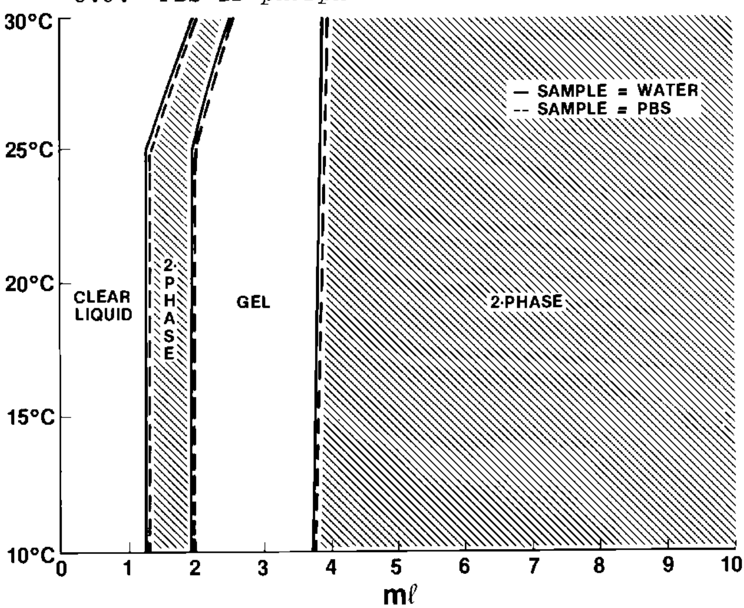

FIGURE 4. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 14.1; 40% emulsifier 3, E.O. = 12.0.

that form at higher sample loads. Again, we have empirically determined that a cocktail using a emulsifier with an HLB value greater than 14.1 forms even more viscous, unusable gels.

Surfactant manufacturers produce a limited number of emulsifiers with HLB values along the continuum between 11 and 14. The most popular of these are nonylphenol ethoxylates with 9 to 10 moles of ethylene oxide (E.O. = 9 to 10; HLB 12.9 to 13.5) such as Triton*N-101, Surfonic[1] N-95, Surfonic[1] N-100, Igepal[2] CO-630, Sterox[3] NJ, Polytergent[4] B-350, T-DET-N[5] 9.5, and Alkasurf[6] NPX. Figure 5 shows a phase diagram of a cocktail using such an emulsifier system.

Figures 6 through 15 are phase diagrams of cocktails prepared by blending the emulsifiers used in cocktails of Figures 3, 4, and 5 to achieve HLB values in the range from 11.8 to 13.7. All of the cocktails have a total emulsifier content of 40% by weight. One observes several important features when examining these phase diagrams. First the clear liquid region expands as the HLB value increases from 10.9 to 12.3. There is negligible gel formation in this range. After reaching an HLB value of 12.5, the clear liquid region regresses to about 15% sample load (1.5 - 2.0 ml/10 ml cocktail) at 25°C and remains constant as the HLB value increases all the way to 14.1. In this same range of HLB 12.5 to 14.1, the gel region appears and becomes more stable with increasing HLB value. Finally, the gels become so viscous that complete mixing cannot take place.

Counting efficiencies of the cocktails represented in Figures 3 through 15 are identical with each other at any given sample load where they are homogeneous preparations: For example, counting efficiency of a 2% aqueous sample is 47%, of a 13% sample is 38%, of a 42% sample is 23% and of a 50% sample is 20%. The maximum Figure of Merit value occurs about 7 to 8 ml of aqueous sample in 10 ml of cocktail for those cocktails with sufficient sample capacity. For those cocktails of more limited sample capacity, the maximum Figure of Merit occurs at the maximum sample load.

*Triton is a trademark of Rohm and Haas Company.
[1]Surfonic is a trademark of Jefferson Chemical Company.
[2]Igepal is a trademark of GAF Corporation.
[3]Sterox is a trademark of Monsanto Company.
[4]Polytergent is a trademark of Thompson-Hayward Chemical Company
[5]T-DET-N is a trademark of Olin Corporation.
[6]Alkasurf is a trademark of Alkaril Chemicals Limited.

Some phase behavior does not depend on HLB value but rather properties of the emulsifier itself. Figures 8 and 9, or 12, and 13 are phase diagrams of cocktails which have the same HLB value achieved by different blends. The blends represented by Figures 8 and 9 have similar phase behavior with water samples, but major differences in phase behavior toward buffered saline solution, PBS. The cocktail using an emulsifier with a long polyethoxy chain (Figure 8) has better salt capacity. This suggests that at a given HLB value, a blend of nonionic emulsifiers with one emulsifier having a long polyethoxy chain would produce more favorable salt solution capacity than a cocktail with a blend of emulsifiers of medium length polyethoxy chains.

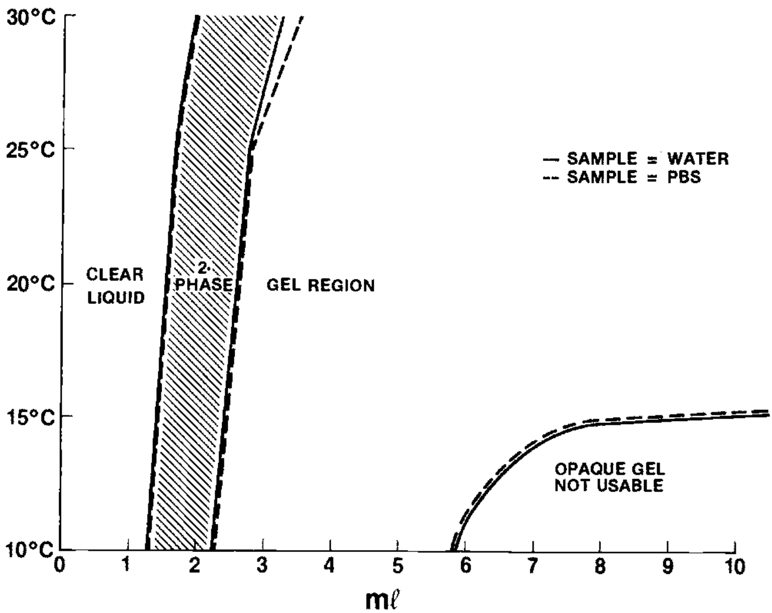

FIGURE 5. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 13.1; 40% emulsifier 2, E.O. = 9.5.

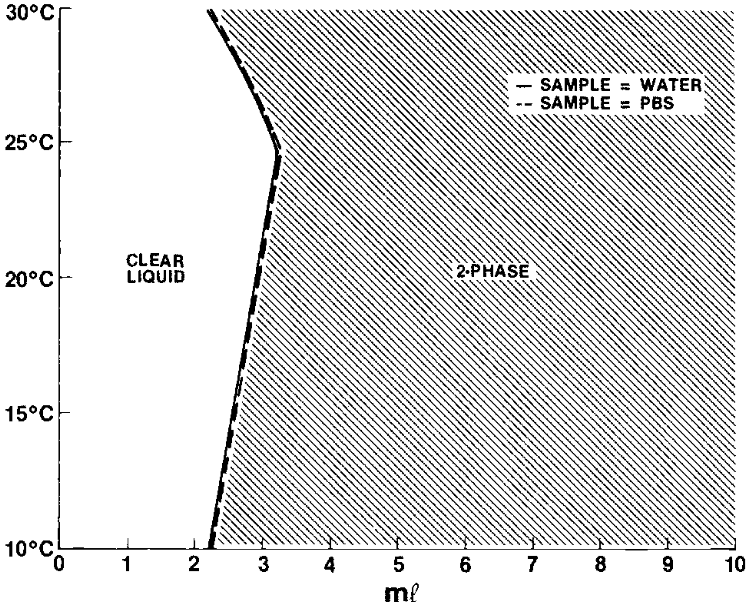

FIGURE 6. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 11.8; 27% emulsifier 1, E.O. = 6, 13% emulsifier 2, E.O. = 9.5, PBS is phosphate buffered saline solution.

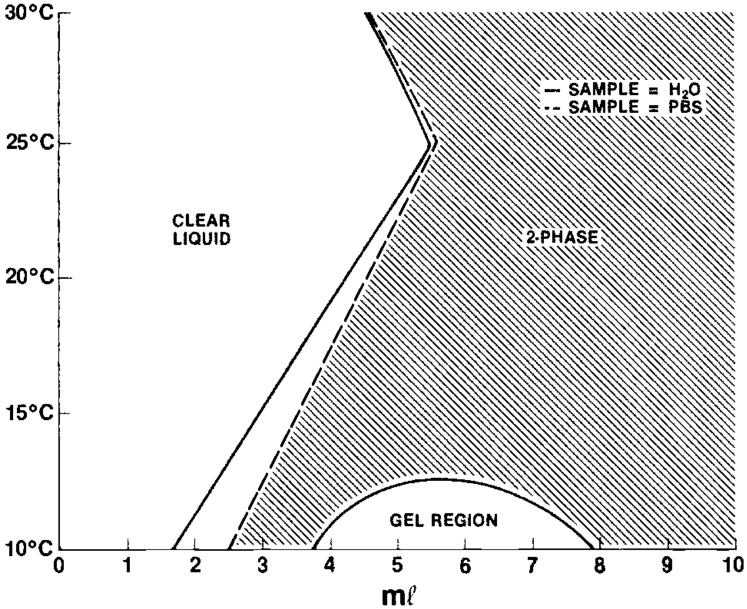

FIGURE 7. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 12.1; 20% emulsifier 1, E.O. = 6.0, 20% emulsifier 2, E.O. = 9.5.

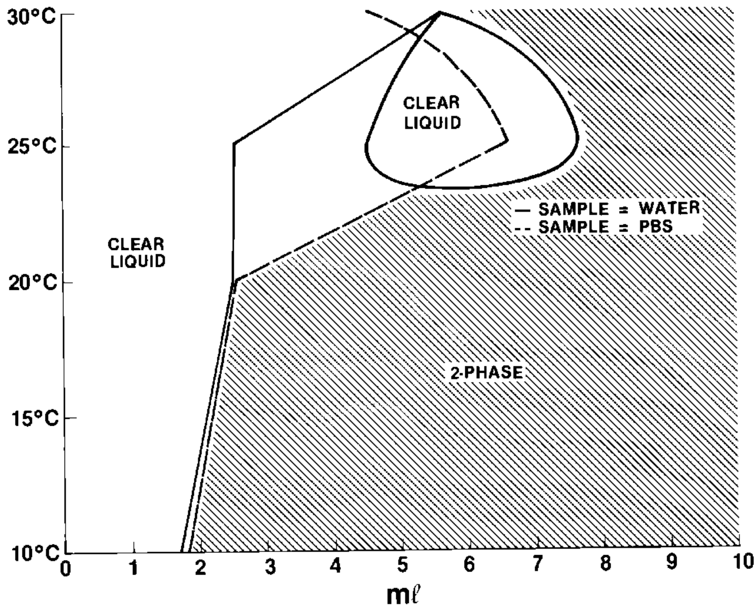

FIGURE 8. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 12.3; 27% emulsifier 1, E.O. = 6.0, 13% emulsifier 3, E.O. = 12.0.

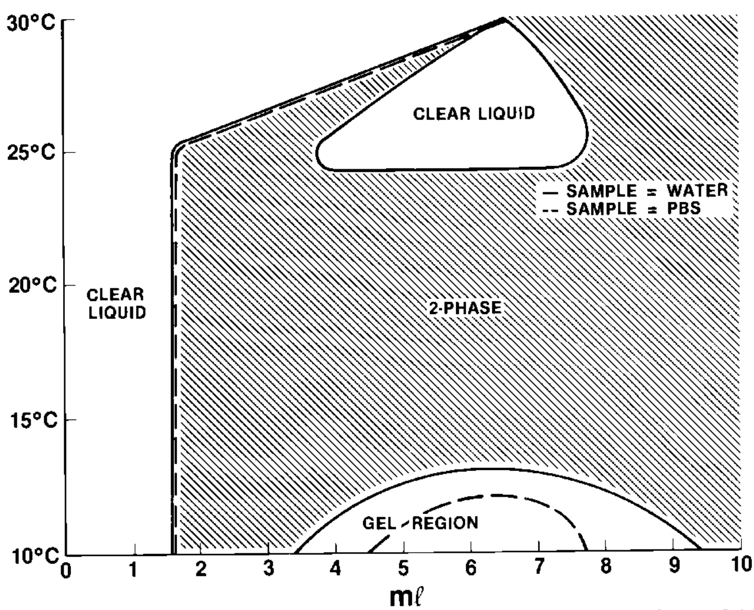

FIGURE 9. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 12.3, 17% emulsifier 1, E.O. = 6.0, 23% emulsifier 2, E.O. = 9.5.

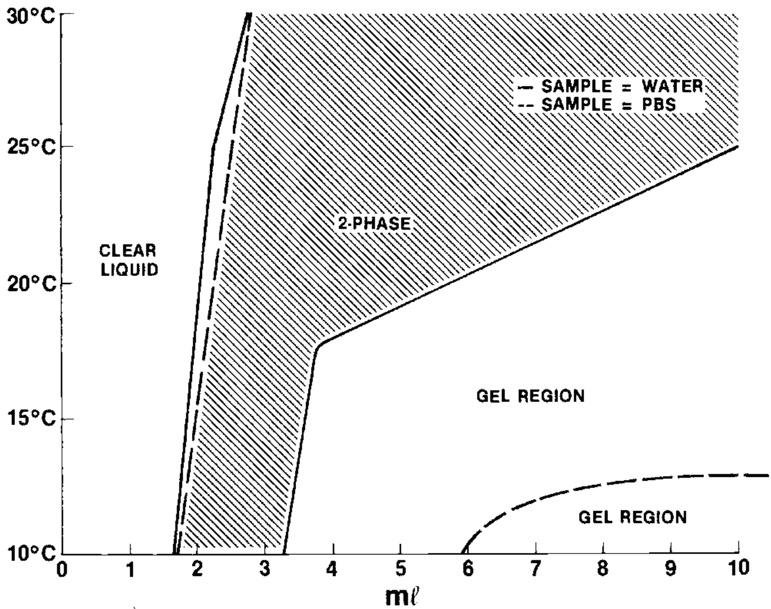

FIGURE 10. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 12.5, 13% emulsifier 1, E.O. = 6.0, 27% emulsifier 2, E.O. = 9.5.

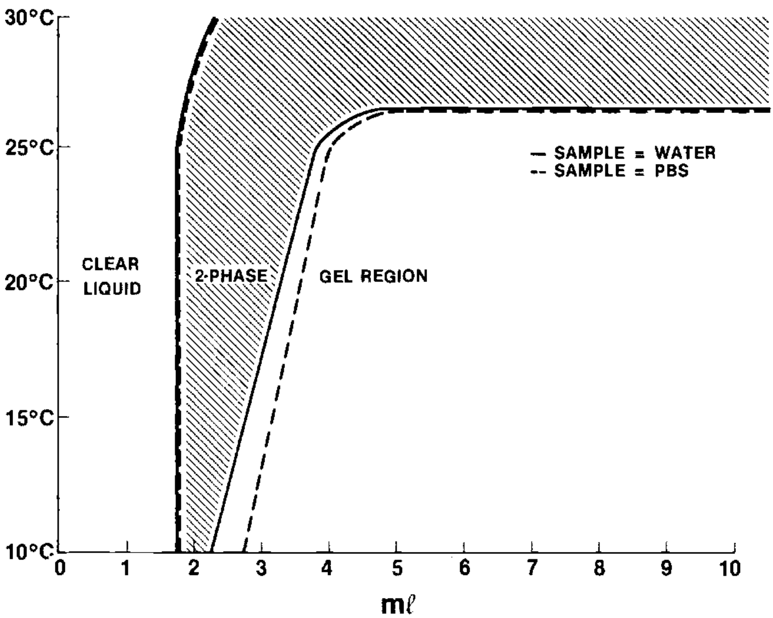

FIGURE 11. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 12.9, 20% emulsifier 1, E.O.= 6.0, 20% emulsifier 3, E.O. = 12.0.

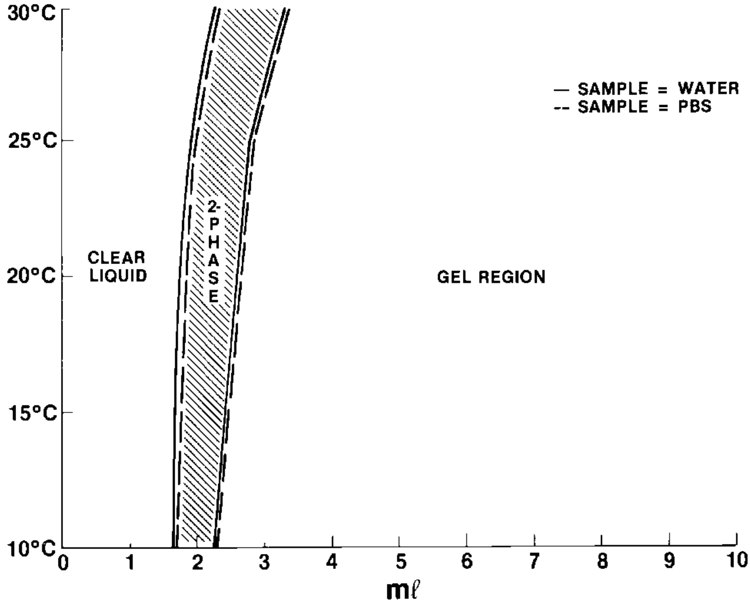

FIGURE 12. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 13.3, 13% emulsifier 1, E.O.= 6.0, 27% emulsifier 3, E.O. = 12.0.

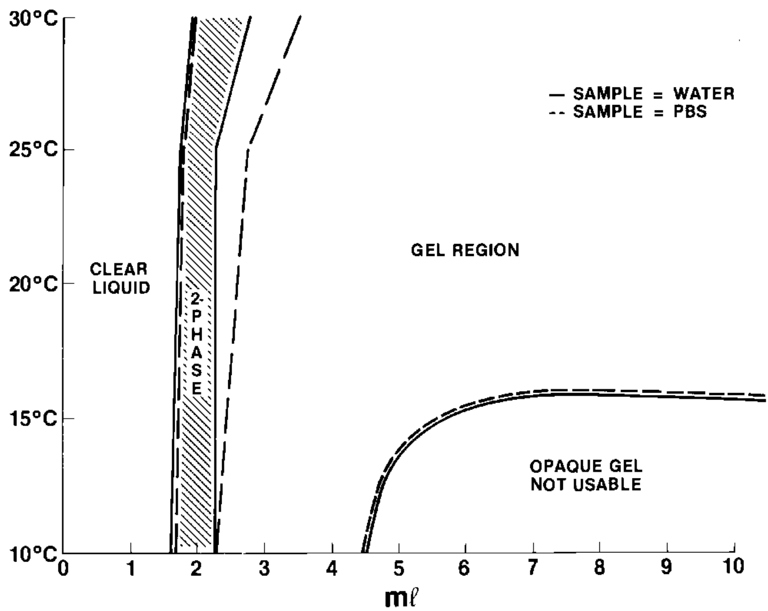

FIGURE 13. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 13.3, 32% emulsifier 2, E.O.= 9.5, 8% emulsifier 3, E.O. = 12.0.

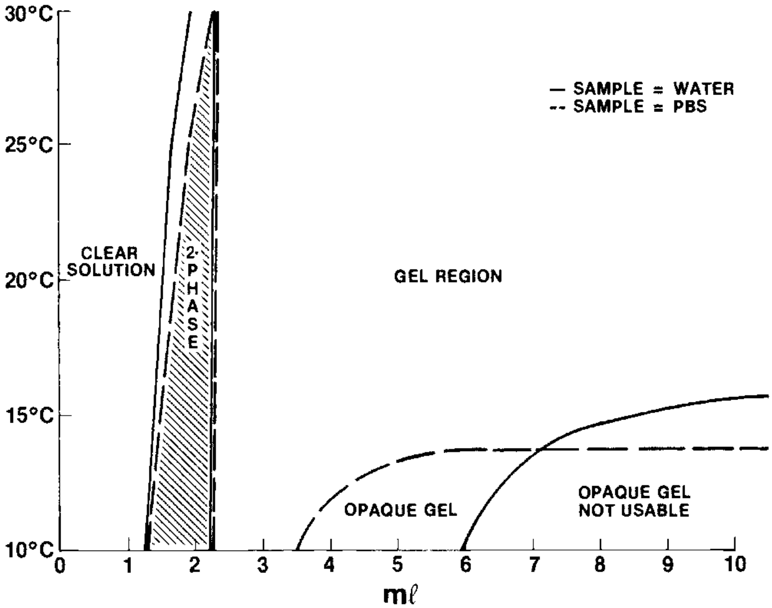

FIGURE 14. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 13.5, 27% emulsifier 2, E.O. = 9.5, 13% emulsifier 3, E.O. = 12.0.

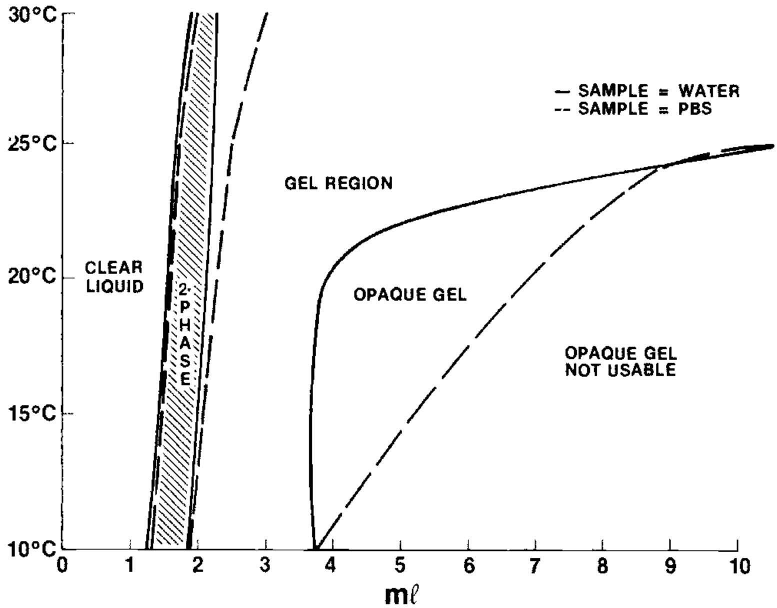

FIGURE 15. Phase diagram of ml sample in 10 ml of cocktail. Formulation: HLB = 13.6, 20% emulsifier 2, E.O. = 9.5, 20% emulsifier 3, E.O. = 12.0.

The cocktails represented by Figures 12 and 13 have one very significant difference although they both have the same HLB value. The cocktail represented by Figure 12 has no unusable opaque gel region. This can be attributed to the presence of an emulsifier with a short polyethoxy chain, E.O. = 6.0. In fact, all the cocktails made exclusively with emulsifiers of longer polyethoxy chains of E.O. = 9.5, or E.O. = 12.0 (see figures 5, 13, 14, and 15) have unusable opaque gel regions.

In summary, blending emulsifiers allows one to achieve a wide variety of HLB values in contrast to the few HLB values available with emulsifiers produced commercially. One can adjust the performance of a cocktail for either a wide clear liquid region or a high sample capacity gelling region by changing the HLB value. In addition, blending specific long chain or short chain emulsifiers can improve the usuable region of the cocktail by improving salt capacity or eliminating opaque regions.

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REFERENCES

Birks, J.B. (1964). In "The Theory and Practice of Scintillation Counting," pp, 278-282, and pp. 361-366. Pergamon, Oxford.

Meads, R.C., and Stiglitz, R.A. (1962). *Int. J. Appl. Radiat. Isotop.* 13, 11.

Lieberman, R., and Moghissi, A.A. (1970). *Int. J. Appl. Radiat. Isotop.* 21, 319.

Griffin, W.C. (1949). *J. Soc. Cosmet.Chem.* 1, 311.

Griffin, W.C. (1954). *J. Soc. Cosmet.Chem.* 5, 249.