

DESIGNING IMPROVED LIQUID SCINTILLATION COUNTING COCKTAILS WITH
THE AID OF THE DOMINANT-PHASE THEORY OF MICROEMULSIONS

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ABSTRACT

The most satisfactory physical state for emulsion liquid scintillation counting (ELSC) is a transparent, macroscopically one-phase mixture of low viscosity known as a microemulsion. Microemulsions are thermodynamically stable and as a result give stable counting. Most ELSC cocktails form microemulsions when 10% v/v water is added, but with larger percentages of water they form viscous mixtures known as gels. These gels can give good counting results but are less reliable than microemulsions. The Dominant-Phase Theory of Microemulsions (DPTM) shows that gels can be transformed into microemulsions by the addition of suitable cosurfactants and indicates the chemical form that these cosurfactants should have. This is possible because, according to the DPTM, the most important factor determining the physical state of the mixture is the stretching force acting on the emulsifier molecules. This force is produced by the opposing attractions for the emulsifier of the separate water-rich and oil-rich regions in the mixture. The DPTM postulates that in a microemulsion this stretching force is small and as a result the emulsifier molecules are subject to little restraint, giving a mixture of low viscosity, whereas in a gel the stretching force is large, resulting in a mixture of high viscosity because the motion of the emulsifier molecules is restricted. The DPTM postulates that a cosurfactant produces its effect by modifying the stretching force. Thus, if a cosurfactant is of such a nature that it dissolves mainly in the water-rich region of the mixture, it changes the solvent properties of this region and thus either reduces or increases the attraction of this region for the emulsifier molecule. Conversely if the cosurfactant dissolves mainly in the oil-rich region, it will modify the solvent properties of this region and so alter the

attraction of this region for the emulsifier molecules. Either of these effects alter the net stretching force acting on the emulsifier molecules. For high efficiency counting, the oil and all cosurfactants and emulsifiers in the mixture must contain a benzene ring in their molecular structure. This ensures that the energy of radioactivity decay is transmitted as efficiently as possible to the primary scintillator. The application of these ideas is illustrated by a description of the development of an ELSC mixture for the high efficiency, high merit value and stable counting of up to 30% sodium hydroxide aqueous solutions using toluene as the oil and Triton X-100 as the emulsifier, with 2-phenylethanol and DL-2-hydroxy-2-phenyl acetic acid (mandelic acid) as cosurfactants.

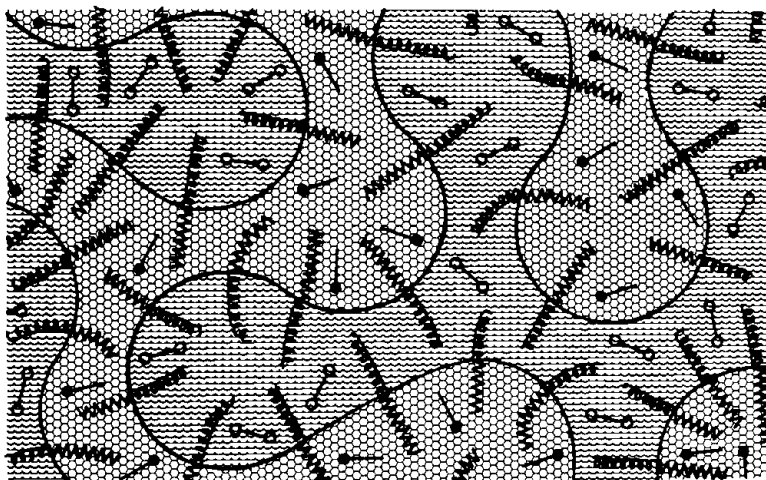
INTRODUCTION

The development of ELSC cocktails has been hampered in the past by the immature state of emulsion theory. For example, Ewer and Harding¹ stated '... there is no coherent theory which will permit... the rational design of 'ideal' scintillation solvents...' A large amount of work has been devoted since early this century to the study of microemulsions. This latter work has produced a number of well-publicized theories^{2,3,4} but, like Ewer and Harding, we found that attempts to apply these theories to the development of scintillation solvents often produced quite different results from those expected. An effective theory of microemulsions would obviously offer many advantages, and for this reason, an experimental and theoretical study of emulsions was pursued concurrently with the development of ELSC liquids. The results of this study, together with the wealth of good experimental evidence obtained in the past by other workers such as Winsor⁴, led to the Dominant-Phase Theory of Microemulsions⁵. This theory has proved to be an effective tool and the way in which it has successfully solved the particularly difficult problem of counting ¹⁴C dissolved in concentrated sodium hydroxide solutions is described here.

According to earlier theories (The Mixed Film Theory² and the 'R' Theory⁴) microemulsions are considered to be of similar structure to macroemulsions in that they consist of droplets of oil suspended in a

continuous medium of water or droplets of water suspended in oil. These are known respectively as oil-in-water (o/w) microemulsions and water-in-oil (w/o) microemulsion. The droplets are considered to be stabilized by a surface layer of emulsifier and cosurfactant. Thus, the essential difference between a microemulsions and a macroemulsion is supposed to be only the size of the suspended droplets. More recently, Friberg³ has pointed out that since the emulsifier and cosurfactants are normally soluble in the oil, a separate surface film of emulsifier and cosurfactant would be penetrated by the oil. The Dominant-Phase Theory extends Friberg's logic by proposing that the mutual solubility of the hydrophilic and lipophilic parts of the emulsifier in the water and oil respectively is the primary function controlling the structure formed. To explain the observed properties in terms of this function, it is necessary to assume that the emulsifier must extend both to the middle of the droplets and throughout the continuous medium in a microemulsion. Such a structure is not a new idea. Ewer and Harding¹ proposed a similar structure for their Reticular Scintillant which is a microemulsion. A microemulsion thus consists of an oil-rich region permeated throughout by the lipophilic part of the emulsifier molecules and a water-rich region permeated throughout by the hydrophilic part of the emulsifier molecules. It is customary to call such regions pseudophases, so the DPTM proposes a bipseudophase structure for microemulsions (Figure 1). The bicontinuous structure of microemulsions proposed by Scriven⁶ is a similar type of structure in that no distinction can be made between the oil and water in terms of one being dispersed and the other continuous. However, Scriven⁶ did not make any proposal for how the emulsifier and cosurfactants are distributed. He simply showed how both oil and water could be continuous. The problem with such a bicontinuous structure is that it is difficult to imagine how two distinct and separate types of microemulsion corresponding to o/w and w/o can exist at the same fixed ratio of oil to water. Such an occurrence has been frequently reported and indeed is shown here in Figures 4, 6 and 7. All theories except the DPTM refer to this phenomenon as the 'inversion' of microemulsions and assume that the difference between the two types is that one is oil-in-water and the

THE STRUCTURE OF MICROEMULSIONS ACCORDING TO
THE DOMINANT-PHASE THEORY



THE BIPSEUDOPHASE STRUCTURE:
SIMILAR TO BICONTINUOUS STRUCTURE







 oil,
  water,
  lipophilic part of emulsifier molecule,
  hydrophilic part of emulsifier molecule,
  lipophilic-type cosurfactant,
  hydrophilic-type cosurfactant.

Figure 1. The morphology of the interfacial regions between the pseudophases is likely to show many variations according to the composition of the mixture, as in the bicontinuous structure described by Scriven⁶, and is of little importance for either practical or theoretical calculations. The essential features are (i) the emulsifier molecules effectively penetrate throughout both pseudophases (ii) a hydrophilic-type cosurfactant is principally confined to the water-rich pseudophase (iii) a lipophilic-type cosurfactant is principally confined to the oil-rich pseudophase (iv) neither type of cosurfactant is concentrated at the interface.

other is water-in-oil. Exactly how this inversion occurs is the subject of some debate.

The Dominant-Phase Theory provides an explanation for these observations which is not dependent on the overall shapes of the pseudophases. The explanation is based on the idea that an emulsifier molecule behaves thermodynamically as a macromolecule. This means that the hydrophilic part of the emulsifier molecule can dissolve in the water in essentially the same way it would if it was not connected to the lipophilic part of the molecule. Conversely the lipophilic part can dissolve in the oil. The two parts are joined in the emulsifier molecule and so a microemulsion forms when a bipseudophase structure is the lowest possible free energy state for the system. The situation is not quite as simple as this because, for example, the attraction of the oil for the hydrophilic part of the emulsifier molecule may be considerable and this will have an effect. An attempt has been made⁵ to provide an analysis that takes account of these complicating considerations.

It is not easy to apply such a complex model to practical problems and it is difficult to give simple explanations based on it. An intimate knowledge of the mutual interactions of all the components, such as their mutual solubilities, is required if such a model is to be used effectively. This information is not readily available. For these reasons, it has been found useful to plan experiments and explain results using the much simpler concept of dominance. This is an artificial concept in the sense that it does not describe what actually exists in a microemulsion. Nonetheless, it generally describes what appears to exist and provided it is not taken literally, it is a very useful tool. It is also the original concept that led to the complete DPTM and gave the theory its name.

The concept of dominance originates from the observation that the only significant difference between the two apparently different types of microemulsions (o/w and w/o) is to be found in the relative magnitudes of the attractions of the oil and the water for the emulsifier. Thus, the type of microemulsion normally described as oil-in-water is most easily formed with a predominantly hydrophilic emulsifier and more water than oil (Figure 2). Here the attraction of

the water for the emulsifier is likely to be greater than the attraction of the oil. Conversely, the type of microemulsion described as water-in-oil is most easily formed with a predominantly lipophilic emulsifier and more oil than water, so here the attraction of the oil for the emulsifier will be greater than the attraction of the water. Since the DPTM is so conceptually different from conventional thinking, it is useful to introduce a different nomenclature for these microemulsions. When the water exerts the greater attraction for the emulsifier the microemulsion is called a water-dominated microemulsion (WDM) and when the oil exerts the greater attraction, the microemulsion is called an oil-dominated microemulsion (ODM). It is important to realize that all possible intermediate forms exist so that the WDM and ODM merely represent the two extreme conditions for the formation of the one type of microemulsion. A distinction is made between ODMs and WDMs simply because the conditions under which a microemulsion may form are most easily satisfied when one of the phases, oil or water, exerts a much greater attraction for the emulsifier than that exerted by the other phase. For this reason, it is easier to formulate a WDM or an ODM than an intermediate form. Why this is so may be understood from a consideration of the structure and composition of the ELSC samples.

The universally recommended composition for ELSC is toluene: Triton X-100 (2:1) containing 10% by volume of aqueous sample. This represents an oil:water:emulsifier ratio of 6:1:3 by volume and evidently this composition forms a very stable microemulsion. Figure 3a shows the probable structure of such a microemulsion. The emulsifier is shown uniformly distributed throughout the mixture whilst the oil and water are segregated. Triton X-100 is very soluble in toluene and so behaves as a predominantly lipophilic emulsifier in this system. Therefore, the concentration profile shown will represent a stable configuration because most of the Triton X-100 is in the oil-rich region. In addition, the emulsifier is required to permeate throughout the more voluminous oil pseudophase as well as throughout the water pseudophase and this condition will be more easily satisfied if most of the emulsifier is in the oil.

The water will only exert a moderate force on the emulsifier

THREE DIMENSIONAL PHASE DIAGRAM SHOWING REGIONS IN WHICH
MICROEMULSIONS AND GELS ARE MOST FREQUENTLY FOUND

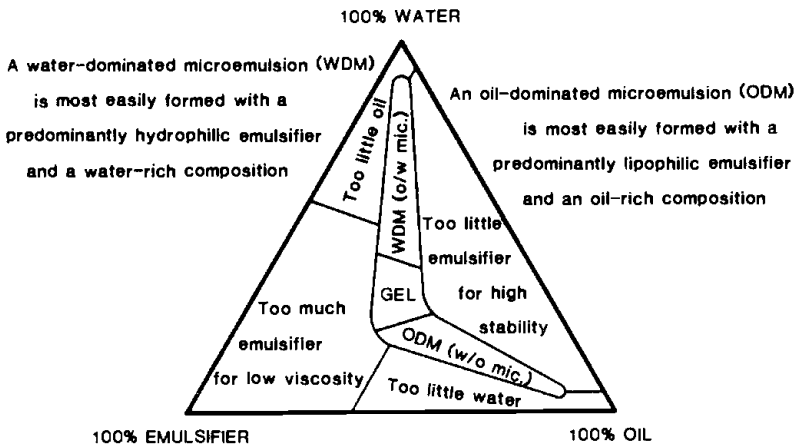


Figure 2. The region in which stable microemulsions are most easily formed is a boomerang-shaped area which is probably related to the amount of emulsifier required to penetrate the two pseudophases at a stable density. When less emulsifier is present, the reduction in the free energy of the system resulting from the hydrophilic part of the emulsifier being in solution in the water and the lipophilic part being in solution in the oil is generally insufficient for a uniform microemulsion to be the minimum free energy configuration. In the regions marked 'too little oil' and 'too little water' it is not physically possible for the emulsifier to extend throughout both phases to form a bipseudophase structure.

molecules (denoted by the arrows) because only a small amount of it is in the water and so the stretching force on the emulsifier molecules will be small. This is why a fluid microemulsion is formed. Adding more water will result in the formation of a gel as indicated in Figure 3b. By analogy, WDMs are most easily formed with a predominantly hydrophilic emulsifier at high water contents.

The impression that there are two types of microemulsion has to be considered as a misconception although it has persisted for so many years that it is now very firmly entrenched indeed. An example of the difficulty created by the proposal that there are two types of

DIAGRAMMATIC EXPLANATION FOR THE OBSERVATION THAT AN ODM IS MOST EASILY FORMED WITH A PREDOMINANTLY LIPOPHILIC EMULSIFIER AND AN OIL-RICH MIXTURE

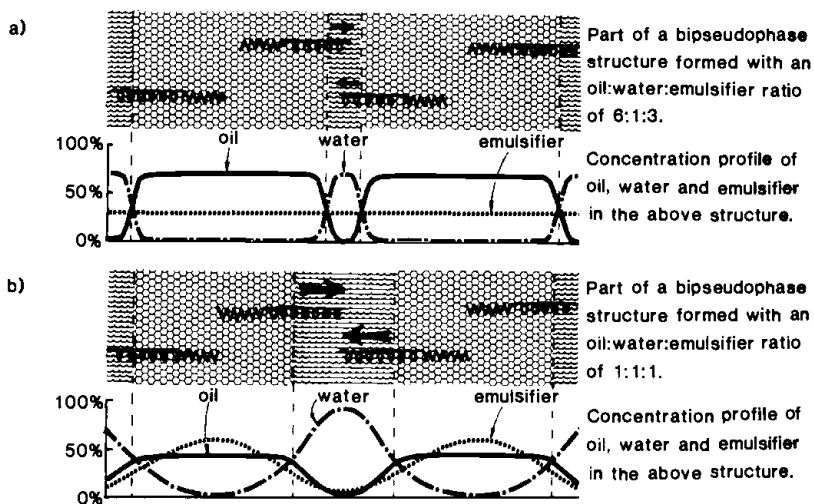


Figure 3. The curves shown in the lower section of each part (a and b) represent the changes in concentration of the three components that are encountered on passing in the horizontal direction through the diagram above. These upper diagrams represent magnified portions of bipseudophase structures of the type shown in Figure 1. The heavy arrows denote a very simplified representation of the attraction of the water for the emulsifier, the larger arrows signifying a greater attraction.

(a) Only a small proportion of the emulsifier is in the water. Therefore only a small attractive force can be exerted. No more of the emulsifier moves into the water because if it did its concentration in the water would rapidly rise. This, in turn, would decrease the attraction of the water-rich pseudophase for the emulsifier.

(b) When more water is added, the water-rich pseudophase exerts a greater attraction for the emulsifier, drawing more of it into the water. This results in the attraction of the water acting on a larger proportion of the emulsifier and so a greater net attraction at equilibrium. Since the oil is the dominant phase, it is inherently able to exert an equal opposing attraction for the emulsifier, although this will only be exerted if the emulsifier is drawn near the interface. The result is that the emulsifier molecules experience a stretching force which constrains their motion and a gel is formed.

microemulsion is that of systems which form a continuous microemulsion region from low water contents to high water contents⁸. Which type, o/w or w/o do they represent? One approach has been to divide the continuous microemulsion region into o/w, bicontinuous and w/o regions on the basis of arbitrary data⁸. The DPTM provides a simpler explanation in that although an ODM and a WDM constitute two extremes, they are extremes of the same basic structure.

These mixtures always contain a fourth component (in addition to oil, water and emulsifier) called a cosurfactant and this use of cosurfactants to produce microemulsions over a wide range of compositions is the key to high merit value counting of aqueous samples. The DPTM proposes that cosurfactants may be divided into two classes, the hydrophilic type and the lipophilic type and suggests that they produce their effects by modifying the solubility of the emulsifier molecules in the water-rich or oil-rich regions respectively. They do this by dissolving in more or less true solution in one pseudophase or the other, so modifying its composition. Obviously this classification represents two extremes and many cosurfactants will dissolve partially in one pseudophase and partially in the other, but nonetheless, it is useful to make the distinction between these two extremes. This proposal is entirely different from conventional ideas on the mode of action of cosurfactants. It is generally assumed that they associate with the emulsifier in the interface and somehow enhance its action. It will be seen later that this new concept is the key to the effective choice and use of cosurfactants.

Since the magnitudes of the attractions of the oil-rich and water-rich regions for the emulsifier can be altered by the addition of appropriate cosurfactants, it should be possible to form a microemulsion at any ratio of water to oil, provided, of course, that there is sufficient emulsifier present. The experimental results in this paper indeed show that by the application of this type of reasoning, ELSC samples containing any amount of water between 10% and 90% may be converted to microemulsions. Outside these limits, it may not be physically possible for the emulsifier to extend throughout both pseudophases and in addition the component in lowest

concentration may form either micellar or true solutions in the other components. Consequently, stable microemulsions are not found at these extremes of composition. The description that follows of the development of an ELSC mixture for counting concentrated aqueous sodium hydroxide solutions illustrates how the foregoing principles are applied in practice.

EXPERIMENTAL

Aqueous sodium hydroxide solutions of concentrations from 5% to 30% were microemulsified with toluene: Triton X-100 (2:1) containing 5 g/l 2,5-diphenyloxazole (PPO) by the addition of cosurfactants. For reasons explained below, it was found necessary to add two cosurfactants to form microemulsions of sufficient stability for counting at high merit values. These two cosurfactants were 2-phenyl ethanol and the sodium salt of mandelic acid (sodium mandelate). To demonstrate the individual effects of these cosurfactants and to show why both were necessary, phase diagrams were mapped using toluene: Triton X-100 (2:1), water and one cosurfactant, as the three variables (Figures 4,5). The situation is also somewhat complicated by the fact that sodium hydroxide has a cosurfactant effect. A phase diagram showing this was also mapped (Figure 6).

A series of phase diagrams were prepared showing the effect of partially neutralizing the sodium hydroxide in the counting samples with mandelic acid (Figure 7). Finally the amount of 2-phenyl ethanol, it was necessary to add to such samples to form ODMs suitable for counting was determined. This simplified approach was adopted because the number of phase diagrams necessary to investigate the system proliferates exponentially with each additional cosurfactant that is added. The addition of 2-phenyl ethanol alters the balance of attractions for the emulsifier in favour of the oil (Figure 4) and so when added to these samples transforms gels and WDMs into ODMs. Hence, 2-phenyl ethanol was added to these samples at 20°C until just sufficient had been added to transform the sample into an ODM. If the sample was already an ODM, no 2-phenyl ethanol was added. Then the samples were cooled to 11°C and more 2-phenyl ethanol added if necessary to again form ODMs. Finally, these samples were again

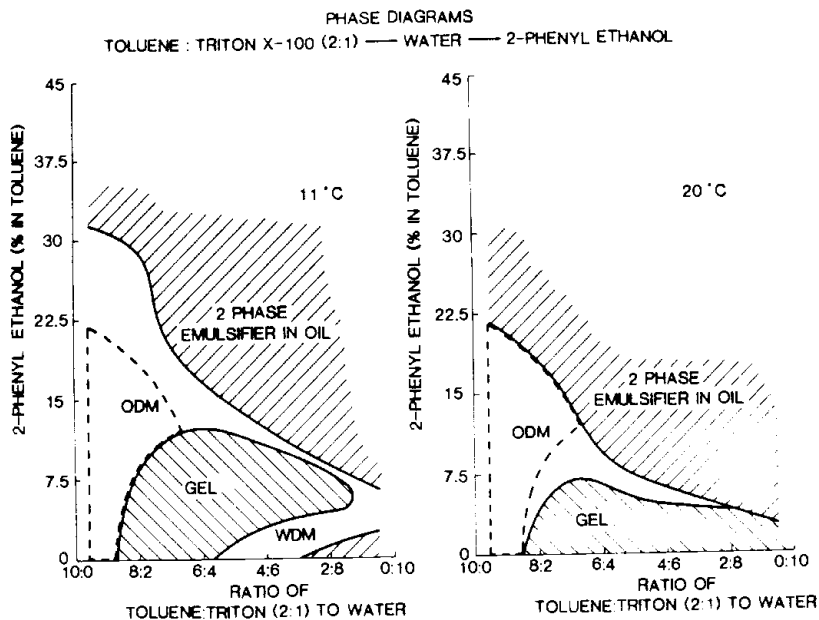


Figure 4. The diagrams were mapped using 113 samples of compositions evenly distributed over the range shown. The region enclosed by the broken line shows the compositions of samples that were microemulsions at both temperatures.

equilibrated at 20°C to see if they remained as ODMs. The detailed data is not given because it is very complex to describe and the net result was simply that the addition of 9% of 2-phenyl ethanol to the toluene: Triton X-100 (2:1) greatly improved the stability of the counting samples to temperature changes and virtually eliminated alkaline degradation of the PPO. In the absence of 2-phenyl ethanol, this degradation rapidly produced a brown discoloration which resulted in colour quenching and a fall in count rate. The samples used to prepare the phase diagrams were mixed in 22 ml screw-capped counting vials by shaking and had a total volume of 10 ml plus cosurfactants. They were stored at the relevant temperature for at least 24 hours with occasional shaking before noting the physical state. They were also re-examined after several weeks to ensure equilibrium had been

reached.

These measurements made it possible to choose a composition that would probably be suitable for counting a wide range of samples. The composition chosen was 0.25 g mandelic acid multiplied by the percentage composition NaOH per 10 ml of aqueous sample. Also 0.9 ml of 2-phenyl ethanol was added per 10 ml of toluene: Triton X-100. The quantities were chosen as a compromise that seemed most suitable for all aqueous sample to scintillation fluid ratios. In fact,

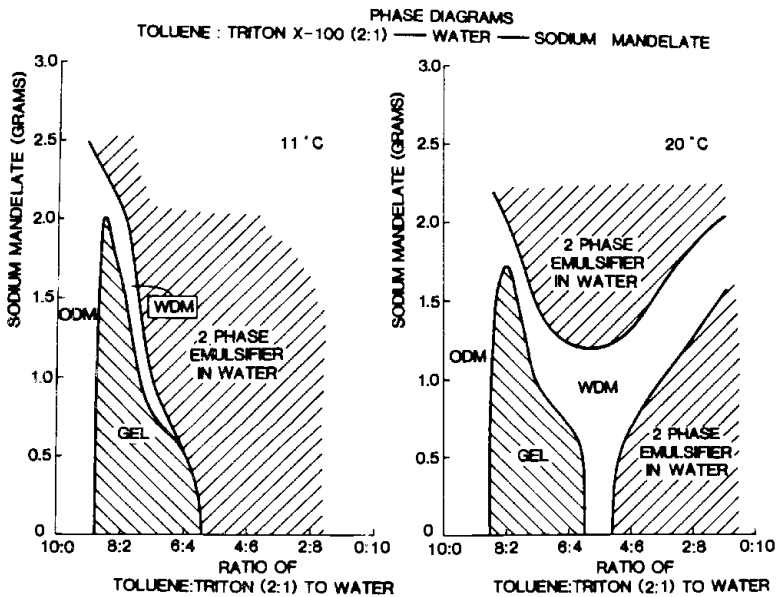


Figure 5. The diagrams were mapped using 195 samples of compositions evenly distributed over the range shown.

satisfactory results were obtained with all the concentrations of sodium hydroxide tested except 5% and 10% NaOH aq. It was necessary to add 20% more mandelic acid to these concentrations. The 5% NaOH aq. also required sodium mandelate and less 2-phenyl ethanol (Table 1).

For high accuracy in counting, it is necessary to know the precise amount of radioactive aqueous sample that is added to the counting vial. Weighing is more accurate than measuring the volume of the sample so the amount of aqueous sample was recorded in grams. Small variations in the amount of scintillation fluid added did not

significantly affect the observed count rate so it was pipetted into the vial and its volume recorded. For this reason, the ratios of scintillation fluid to sample shown in Figure 8 and Table 1 refer to a volume (ml) to weight (g) ratio. The sodium hydroxide solutions all contained $\text{Na}_2^{14}\text{CO}_3$ at a specific activity of 737.3 ± 11 S.D. (6) kBq/l. This activity was assayed by the internal standard method of quench correction using Amersham International CFR6 n[^{14}C] hexadecane reference standard and Packard Inst. Co. ES 299 scintillation cocktail⁹.

The performance of the samples was investigated by repeatedly

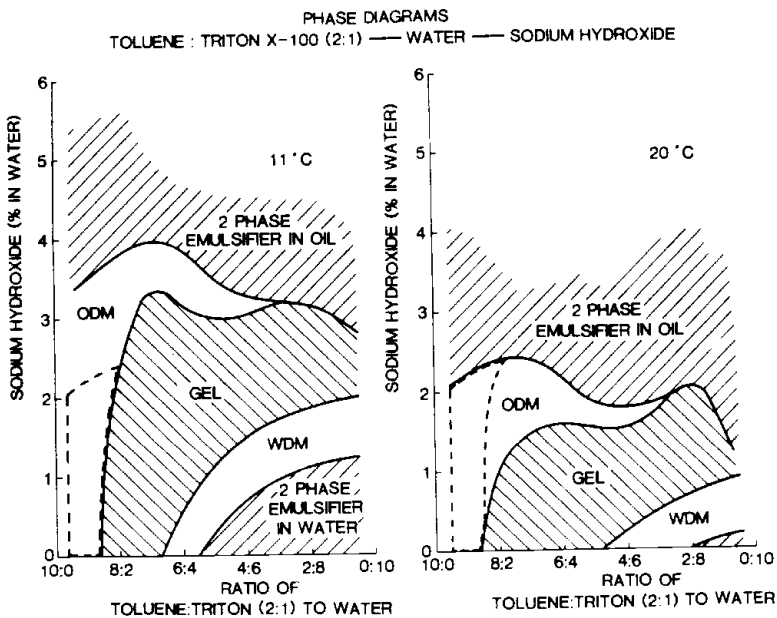


Figure 6. The diagrams were mapped using 127 samples of compositions evenly distributed over the range shown. The region enclosed by the broken line shows the compositions of samples that were microemulsions at both temperatures.

counting the samples at 25°C and 11°C in two different counters over a period of one month. In this way, the stability of the samples and reproducibility of the count rates were investigated. The results for the samples counted at 11°C on a Searle Analytic 92 (G.D. Searle and Co., 2000 Nuclear Drive, Des Plaines, Ill. 60018) are shown in Figure

PHASE DIAGRAMS (20°C) SHOWING EFFECT OF PARTIALLY NEUTRALISING
THE SODIUM HYDROXIDE PRESENT IN ELSC SAMPLES WITH DL-MANDELIC ACID

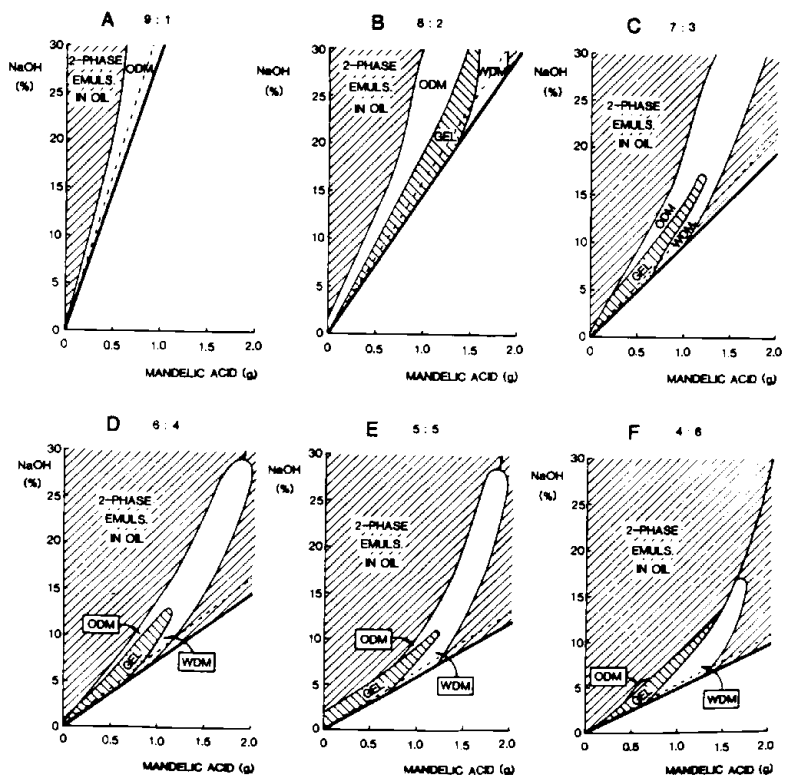


Figure 7. The ratios indicate the relative proportions by volume of toluene: Triton X-100 (2:1) and aqueous NaOH. The samples each contained a total volume of 10 ml plus mandelic acid. Thus A refers to mixtures containing 9 ml of toluene: Triton X-100 (2:1) and 1 ml aqueous NaOH. The broken straight line on each diagram shows compositions containing 0.5% NaOH aq., the remainder having been neutralized by mandelic acid. The heavy straight line shows compositions containing equimolar quantities of NaOH and mandelic acid. Samples containing more mandelic acid than this were not investigated. The number of samples used to map the phase diagrams was 60 (A), 70 (B), 93 (C), 68 (D), 58 (E), and 43 (F). The shaded regions to the right of the microemulsion regions denote two-phase compositions in which the emulsifier was in the water.

MERIT VALUE vs SAMPLE : SCINTILLATION FLUID RATIO
FOR 5% TO 30% NaOH SOLUTIONS

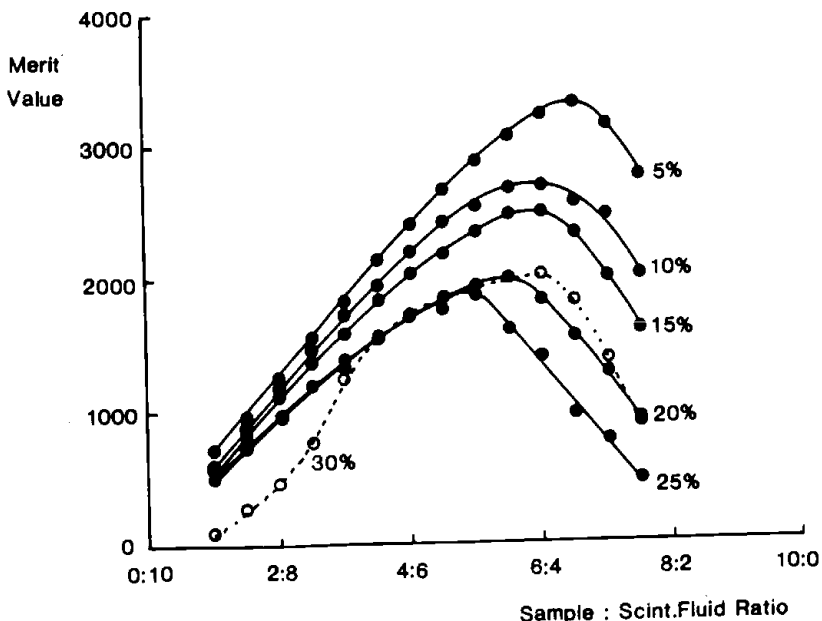


Figure 8. The compositions of the scintillation fluids and samples are shown in Table 1. Each counting vial was counted for 10 min ten or eleven times over a minimum period of a month on the Searle Analytic 92 counter at 11°C. Merit values were calculated as 10 x percentage counting efficiency x weight (g) of the 'sample' ('sample' as defined in Table 1). Standard deviations were calculated and were within the range covered by the circular symbols. The results for 30% NaOH aq. are shown by open circles and a broken line for clarity.

8 and Table 1. Similar results were obtained on a Nuclear Enterprises NE 8312 dual β and γ counter (Nuclear Enterprises Ltd., Sighthill, Edinburgh, EH11 4EY, Scotland). The normal channel settings recommended for ^{14}C on each machine were used in all counting tests and the samples were stored at room temperature between counting sessions.

RESULTS AND DISCUSSION

The phase diagrams. The positions of the boundaries between the

different physical states shown in the phase diagrams were not always distinct experimentally for two main reasons. The first is that the proportion of emulsifier present in the samples decreases as the amount of water increases. This caused the boundaries between physical states in high water-content samples to be somewhat indistinct. The second reason concerns the boundaries to the gel regions. A two-phase region (usually called the lamellar region) is often observed at compositions between those forming microemulsions and gels. When a lamellar region was observed, it was included in the gel regions on the phase diagrams. Sometimes a lamellar region was absent and a continuous smooth change in viscosity between gels and microemulsions was observed. In such cases, the criterion used to distinguish a gel from a microemulsion near the boundaries was the presence or absence respectively of semi-solid lumps in the fluid running down the side of the vial immediately after shaking.

Another feature of the phase diagrams that merits clarification concerns the two-phase regions. When the two phases separate with the emulsifier in one of them the environment of the emulsifier changes. Thus, when the emulsifier is in the oil and a separate water phase forms, the emulsifier enters an environment containing less water than is represented by the overall composition of the mixture. If, for example, the reason for the separation into two phases can be regarded as being caused by the presence of too much water, as, for example, when the ratio of toluene: Triton X-100 (2:1) to water is 5:5 and the percentage of 2-phenyl ethanol in toluene is 20% (Figure 4), then the removal of some of the water into a lower phase will leave a composition containing less water and this will form a stable microemulsion. Therefore, the upper oil phase containing the emulsifier is often an ODM in equilibrium with a lower water phase. For this reason, only part of the water separates as a distinct phase and exactly how much depends on the conditions. Likewise, when the emulsifier is in the lower water phase, this is often a WDM containing some of the oil in equilibrium with an upper oil phase. For this reason, when two phases existed, one of the phases often only represented a small fraction of the total volume. In general, the volume of the emulsifier-free phase was greater the further away the

**Counting Sample Compositions and Results for Highest Merit Value Sample
at Each Concentration of NaOH.**

CONCENTRATION OF AQUEOUS NaOH SOLUTION (%)	WEIGHT (G) OF MANDELIC ACID ADDED PER 10 ML. OF AQUEOUS NaOH SOLUTION	WEIGHT (G) OF SODIUM MANDELATE ADDED PER 10 ML. OF AQUEOUS NaOH SOLUTION	VOLUME (ML) OF 2-PHENYLETHANOL ADDED PER 100 ML. OF TOLUENE:TRITON X-100 (2:1)	RATIO OF SCINTILLATION FLUID TO SAMPLE FOR MAXIMUM MERIT VALUE	COUNTING EFFICIENCY FOR ¹⁴ C (%)	MERIT VALUE
5	1.50	1.00	7	3.5 : 6.5	51.0	3315 ± 17 s.d. (10)
10	3.00	-	9	4 : 6	46.0	2702 ± 57 s.d. (11)
15	3.75	-	9	4 : 6	41.7	2505 ± 45 s.d. (11)
20	5.00	-	9	4.5 : 5.5	36.4	2002 ± 36 s.d. (11)
25	6.25	-	9	5 : 5	37.5	1874 ± 22 s.d. (11)
30	7.50	-	9	4 : 6	33.9	2035 ± 69 s.d. (11)

Table 1. The scintillation fluid was toluene: Triton X-100 (2:1) containing 5 g/l PPO and the amount of 2-phenyl ethanol shown. The term 'sample' refers to the sodium hydroxide solution after the addition of the mandelic acid and sodium mandelate. The sodium hydroxide solutions all contained Na₂¹⁴CO₃ (737.3 ± 11 S.D. (6) kBq/l). Each counting sample had a total volume of 10 ml. Merit values were calculated as described in Figure 8. The scintillation fluid to sample ratios refer to volume (ml) to weight (g) ratios.

composition was from a microemulsion region.

The cosurfactant effect of sodium hydroxide. The effect of sodium hydroxide on mixtures of water and toluene: Triton X-100 (2:1) shown in Figure 6 is related to the well-known 'salting out' effect of electrolytes on aqueous solutions of organic substances such as diethyl ether. An electrolyte diminishes the solubility of diethyl ether in water and this is equivalent to a reduction in the attraction of the water phase for the ether. The hydrophilic part of Triton X-100 contains a series of ether groups so the presence of an electrolyte will also diminish the attraction of water for this emulsifier. Thus, as the concentration of sodium hydroxide increases, the attraction of the water for the emulsifier diminishes and the balance of attraction shifts in favour of the toluene. This causes a

progressive sequence of changes of state between the two extremes represented by a solution of Triton X-100 in water co-existing with a more or less pure toluene phase and a solution of Triton X-100 in toluene co-existing with an aqueous sodium hydroxide phase. Between these two extremes is found the sequence WDM, gel, ODM with the WDM bordering the two-phase region in which the emulsifier is in the water and the ODM bordering the two-phase region in which the emulsifier is in the toluene. This is precisely the mechanism postulated by the DPTM to account for the action of hydrophilic cosurfactants and so it is evident that inorganic electrolytes form part of this class.

The full sequence of this series of changes of physical state appears at high water contents but at low water contents the only one-phase system observed is an ODM. There are two reasons for this. Firstly, Triton X-100 is very soluble in toluene compared with water so that when little water is present it is not capable of exerting a large attraction for the emulsifier relative to that exerted by the toluene. Secondly, since the ratio of toluene to Triton X-100 is 2:1, there are 3 ml of Triton X-100 to 1 ml of water when water forms only 10% of the mixture. Since Triton X-100 consists of 67.4% by weight poly(ethylene oxide) this means that the concentration of the hydrophilic tails in the water pseudophase is high and this in itself will cause the attraction of the water pseudophase for the emulsifier to be small.

A good indication of the stability of a microemulsion is given by observing the effect of temperature changes. This is particularly relevant for ELSC applications since samples are often cooled before counting. The region enclosed by a broken line in Figure 6 shows the restricted range of compositions of samples containing sodium hydroxide that are stable between 11°C and 20°C. Therefore, another cosurfactant must be added if stable microemulsions are to be formed at higher water contents.

The cosurfactant effect of sodium mandelate. Since Triton X-100 is very soluble in toluene and sodium hydroxide reduces the attraction of water for this emulsifier, the most suitable type of cosurfactant to produce stable microemulsions with NaOH aq. solutions would be one which increases the attraction of the water for the emulsifier. The

rationale is that such a cosurfactant would result in a strong attraction for the emulsifier being exerted by both pseudophases and hence it would be very favourably energetically for the emulsifier to be at an oil-water interface. In choosing such a cosurfactant, a knowledge of the DPTM is essential. This theory suggests that the water pseudophase in the type of microemulsion under discussion consists of a solution of the hydrophilic poly(ethylene oxide) part of the Triton X-100 molecule in water. Triton X-100 has a hydrophile-lipophile balance (H.L.B.) of 13.8 and this means it consists of $5 \times 13.8 = 69.0\%$ by weight of poly(ethylene oxide) condensate. The molecular weight of octyl phenol is 212 and so the average molecular weight of the poly(ethylene oxide) part of the molecule is $212 \times 69 / (100 - 69) = 470$. Therefore, it is reasonable to suppose that the water pseudophase will have similar solvent properties to an aqueous solution of poly(ethylene oxide) of average molecular weight 400 (PEG 400). The solubility of sodium mandelate in mixtures of PEG 400 and water is about 430 g/l for ratios between 3:7 and 7:3 but decreases outside this range. The solubility of sodium mandelate in water is 270 g/l and its solubility in PEG 400 is about 50 g/l. It is virtually insoluble in toluene. When sodium mandelate is added to the mixtures in question, it alters the balance of attractions in favour of the water (Figure 5). This is probably because separation of the hydrophilic part of the emulsifier from the water would leave a mixture with a lower solvent capacity for sodium mandelate and this would result in an increase in the total free energy of the system. The net result is that at low water-contents the attraction of the toluene remains dominant but at higher water-contents (at 20°C) WDMS are formed over a wide range. However, on cooling to 11°C the attraction of the water phase for the emulsifier increases and a two-phase system is formed with the emulsifier in the water. Thus, sodium mandelate alone is not sufficient to form the stable microemulsions required for ELSC at high merit values. Also, it is undesirable to neutralize all the sodium hydroxide in the counting samples. Therefore, the effect of partial neutralization was investigated.

The combined cosurfactant effects of sodium hydroxide and sodium

mandelate. Sodium hydroxide decreases the attraction of the water for the emulsifier whilst sodium mandelate increases this attraction. The phase diagrams shown in Figure 7 are, in effect, the result of combining the two. The six phase diagrams were mapped at 20°C. Cooling the samples to 11°C showed again that compositions containing large proportions of water were not microemulsions at both temperatures. This is why 2-phenyl ethanol was needed.

The cosurfactant effect of 2-phenyl ethanol. The effect of 2-phenyl ethanol on mixtures of toluene: Triton X-100 (2:1) and water is shown in Figure 4. This phase diagram is similar to that obtained with sodium hydroxide (Figure 6) but it is important to note that the concentration of 2-phenyl ethanol relative to the toluene is plotted in Figure 4, whereas the concentration of sodium hydroxide relative to the water is plotted in Figure 6. This done because when a cosurfactant is almost completely confined to one phase or pseudophase its concentration in that phase or pseudophase is the relevant parameter. Thus, from Figure 6, it is immediately evident that ODMs form over a wide range of water-contents at 20°C with a concentration of about 1.8% sodium hydroxide in the water.

2-Phenyl ethanol is only slightly soluble in water, whilst it is very soluble in toluene. Therefore, it is likely to be found in the toluene pseudophase. However, it is also very soluble in aqueous solutions of PEG 400. It can, therefore, act as a hydrophilic cosurfactant with Triton X-100, since it can dissolve in the water pseudophase. It is not possible to deduce how it is acting from this evidence but it is probably present in both pseudophases. However, the diagrams show that its effect is to alter the balance of attractions of the oil and water for the emulsifier in favour of the oil and this is the information of practical value. The addition of 2-phenyl ethanol will therefore tend to convert gels and WDMS into ODMs.

The scintillation counting tests. There are two reasons why it is useful to count aqueous sodium hydroxide solutions. The first is that $^{14}\text{CO}_2$ is a ubiquitous substance that is likely to be produced by decolorization procedures¹⁰ even if it is not initially present. The second is that sodium hydroxide exerts a powerful solvent action

on a wide range of organic material. These advantages are lost if the samples are neutralized before counting so the approach adopted here was to neutralize only a part of the sodium hydroxide with mandelic acid. Thus, the amounts of mandelic acid added (Table 1) represent the amounts required to neutralize 79% of the sodium hydroxide in the 5% and 10% NaOH aq. samples and 66% of the sodium hydroxide in the 15% to 30% NaOH aq. samples. Other approaches could have been used. For example, sodium mandelate could have been added instead of mandelic acid. However, the method used was simpler because otherwise, it was first necessary to prepare the sodium mandelate from mandelic acid. Further work will be needed to see if any advantage is to be gained from other compositions.

The addition of mandelic acid to alkaline samples could result in localized acidification of the mixture before uniform solution has been achieved even when the total amount added is insufficient to neutralize all the sodium hydroxide present. This could result in loss of $^{14}\text{CO}_2$ so to check that this was not happening the test samples were prepared using NaOH solutions containing a known amount of $\text{Na}_2^{14}\text{CO}_3$. The details of compositions and the results are shown in Table 1 and Figure 8. Concentrations from 5% to 25% NaOH aq. gave a family of curves whilst 30% NaOH aq. gave a rather different curve. The reason is that this composition is near the limit of solubility of sodium mandelate in the mixtures. Thus, this concentration is the upper limit at which the method is applicable and it is probably wise not to exceed 25% NaOH in practice.

CONCLUSIONS

The mixture described provides a very much improved method for counting low levels of $^{14}\text{CO}_2$ trapped in sodium hydroxide solutions. Previous methods^{9,11} involved trapping in 5% NaOH aq. It was then necessary to count 0.1 ml of this in a 10 ml counting sample containing 0.9 ml water. This gives a merit value for 5% NaOH aq. of 90 calculated as described in the legend to Figure 8 and assuming 90% counting efficiency. The present method is a great improvement on this. The mixture also offers the possibility of taking advantage of the powerful solvent action of sodium hydroxide in preparing extracts

of organic samples for counting. Further testing will be required to evaluate this. Considering the complexity of the mixture required to achieve these ends and the unusual nature of the cosurfactants, it is most unlikely that this problem could have been solved without the aid of the DPTM.

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