Detergent Application of the Measurement of Critical Micelle Concentration

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IN SURFACTANT SOLUTIONS, aggregations of molecules (micelles) form over a rather narrow range called the critical micelle concentration (cmc). The importance of this range has been splendidly illustrated by Preston (25), as shown in Figure 1. Note that at the cmc range the surfactant is at essentially its optimum of activity as measured by a variety of tests. Consequently it might be expected that further knowledge of this critical value for a variety of surfactants could have much potential value.

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Characterization of Micelles

McBain (19) is generally considered the pioneer in this field, and he pictured a micelle as being a regular arrangement of molecules in a palisade structure (Figure 2). Hartley (7) from other evidence considered micelles as being spherical in contour. Micelles start forming before the critical concentration is attained, as shown by McBain's (21) conception (Figure 3).

The shape of micelles has been studied intensively. In addition to the palisade or sphere, other investigators have produced evidence convincing them that micelles have a sandwich structure, are quasi-cylindrical in shape, are disks, rods, sausage-shaped, oblate-spheroids, and so on. Perhaps the chemical structure of the compounds investigated may have some control of micellar shape.

Micelles, in addition to shape, have size; and molecular weight determinations by equilibrium dialysis, X-ray diffraction, and light-scattering studies have shown that surfactants associate in rather definite numbers of molecules per micelle and that the micelle molecular weights vary regularly within a homologous series, generally increasing in size with increasing hydrophobe chain length. For low molecular weight compounds as few as ten molecules are associated while in other cases they exceed a hundred. The micelle molecular weights vary from less than 4,000 to greater than 40,000.

Associated with micelles are gegen ions (ions of charge opposite to that of the long-chain ion within the micelle) as in Figure 3. These affect the properties of the micelles as evidenced, for example, by measurement of conductivity.

Micellar systems are relatively quite stable, capable of being filtered unchanged through very fine-pored filters, and maintain their stability as a result of existing in a lowered energy condition.

Ability to solubilize both liquid and solid organic materials with, or without polar groupings, is a valuable property of surfactants. How this mechanism can result is shown in Figure 2 (13). Certainly, in the course of the detergent operation, solubilization of the oily type of soils occurs in addition to emulsification, helping to produce very stable soil-surfactant systems.

Measurement of Critical Micelle Concentration

A useful definition of cmc (28) is that this is the concentration represented by the point of intersection of lines extrapolating the measured properties of the solution from below and from immediately above the region in which rapid change of slope is observed. A more precise treatment (28) defines cmc as the concentration of solute at which the concentration of micelles would become zero if their concentration were to change at the same rate as it does at a slightly higher concentration.

Methods which have been used for determining cmc are conductivity, density, refraction, pH, X-ray diffraction, surface tension, interfacial tension, bubble pressure, polarographic changes, freezing point, light scattering, dye solubilization, spectral dye changes, equilibrium dialysis, and others. All of these measure change in solution properties, which occurs at a definite concentration change.

A variety of these methods is applicable to either anionic or cationic surfactants, but relatively fewer are adaptable to nonionics. Perhaps the most widely used method is the spectral dye procedure, operated either visually or spectrophotometrically. Because of their nature, nonionic surfactants represent a special case to which the number of applicable methods is considerably reduced: surface tension; interfacial

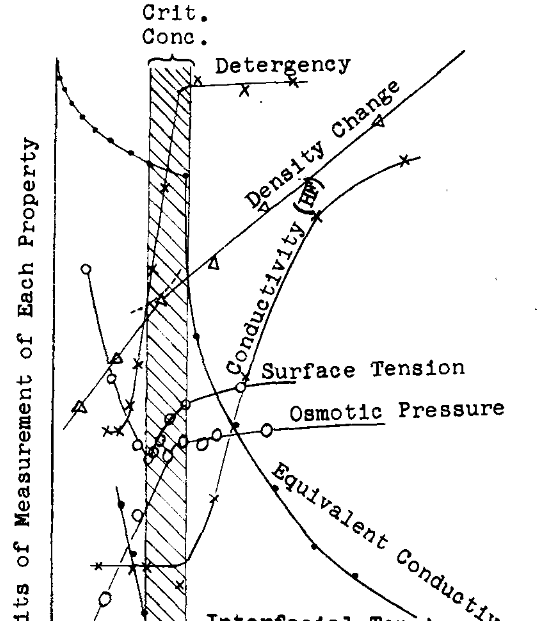


FIG. 1. Physical property curves (25).

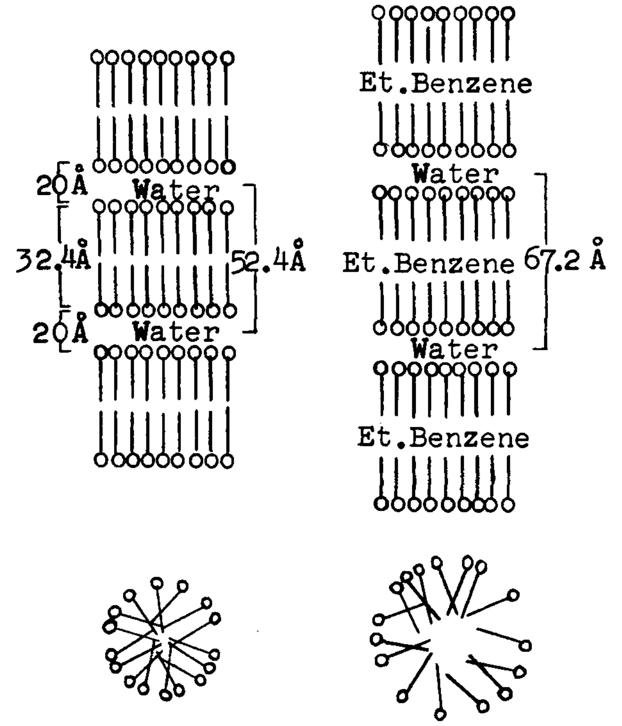


FIG. 2. McBain lamellar micelle, Hartley spherical micelle.

tension; dye solubilization; freezing point; light scattering. The introduction of electrolyte detergent builder products into these systems reduces the desirability of certain methods for measurement.

Conductivity Method. The rate of change in conductivity with variation in concentration is sufficiently marked at the critical concentration that this becomes a valuable method for estimation. The literature abounds in references to the technic, and only one will be given as an example (26).

Necessary to this technic is a constant temperature bath controllable to ±0.005°C., preferably closer. A conductivity bridge operated at 1,000 cycles and of sufficient precision should be chosen. A photoelectric eye indicator may be used for null-point detection. While dip cells of the proper cell constant characteristics have been used, greater precision and/or ease of handling can perhaps be attained by using a special flask cell, such as Shedlovsky's.

Preferred for this method are well purified ionic surfactants, free from extraneous electrolytes. While the effect of builder electrolyte upon a surfactant system can be determined with this equipment, more rapid procedures less liable to distortion are to be preferred. An example of data, using this system, is plotted in Figure 4, showing the extrapolated cmc value.

Refraction Method. Klevens (11) has used this method very satisfactorily. No physical change is made in the system during measurement, thus obviating many of the possible complaints to other procedures. Ordinary refractometers however are unsatisfactory. Klevens uses a Rayleigh-Haber-Löwe type of interferometer. Solutions again should be carefully temperature-controlled, preferably within a ±0.003°C. range.

Spectral Dye Procedure. Corrin, Klevens, and Harkins (1) developed what might be termed the "poor man's" method for measuring cmc. Certainly it eliminated the need for expensive equipment and extremely precise temperature control, required only visual examination of colored solutions using standard laboratory equipment and rapidly providing experimental results. They used a dilute pinacyanole chloride solution (a cationic dye) with anionic surfactants; a color change occurred at the point where micelles just formed. Satisfactory anionic dyes were found for testing cationic surfactant solutions.

Briefly the procedure comprises preparation of a surfactant solution at a concentration above the cmc in 10^{-4} to 10^{-5} M pinacyanole chloride (Eastman), and addition of aliquots of the same strength of aqueous dye solution to the dye-surfactant solution, and the determining of the point at which color changes. This is best done against a white background, using containers of the same dimensions and clarity for observation. Because of the personal element, comparison standards are desirable.

Herzfeld (9) carefully investigated the variables of this system, both visually and photometrically, showing the controls necessary to produce reliable comparative results. The personal element can thus be reduced to a minimum, and more precise measurements made.

The main advantages of the spectral dye method appear to be its speed of operation and application under a wide variety of experimental conditions. Its disadvantages are occasional variation from results obtained by other methods andd lack of application to nonionic surfactants.

Dye Solubilization. Hartley (8) determined the solubilizing effect of surfactant micelles upon trans-azobenzene, and this was applied to the determination of the critical concentration. McBain and co-workers used water-insoluble Yellow AB (20), Orange OT (22) while Kolthoff and Stricks (15) also used trans-azobenzene and dimethylaminoazobenzene.

This method consists of shaking fine crystals of the dye in dilutions of surfactant solution spanning the cmc in a constant temperature bath, removing undis-

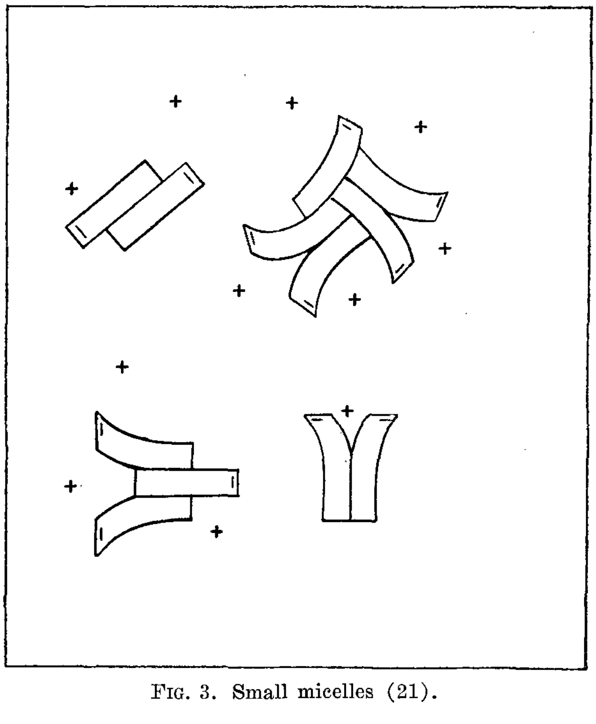


FIG. 3. Small micelles (21).

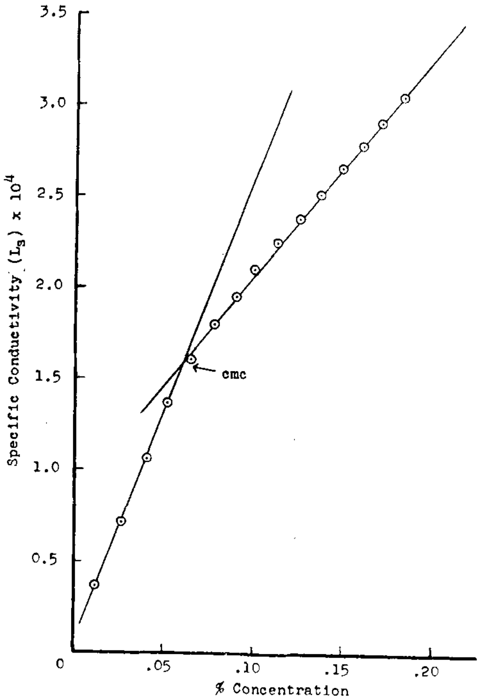


FIG. 4. Determination of cmc value-conductivity method (sodium oleate).

solved dye, and measuring the optical density of the clear solutions. These values are plotted and the intercepts drawn.

Perhaps the greatest difficulty in this method is that various dyes show preferential solubility to certain surfactants. A minor drawback is the time necessary to attain equilibrium though Lambert and Busse (16) overcame this by operating at 50°C. rather than 25°, where they show equilibrium in 15 min.

The advantages of the method are several. It is applicable to all types of surfactants, can be rapid, can be used with surfactant builder systems.

Surface and Interfacial Tension Measurements. Measurement of either surface or interfacial tension are time-consuming but relatively effective methods for determining cmc. Many types of equipment are applicable; the DuNouy tensiometer represents an apparatus generally available for the purpose and no discussion of procedures involved is indicated.

One of the difficulties with the DuNouy method lies in adequate temperature control, but apparatus for this purpose can be constructed. At elevated temperatures, evaporation is also a difficulty, but again this can be corrected.

One of the main advantages of the surface or interfacial tension methods is that all types of surfactants can be evaluated.

Detergent Applications of cmc Measurement

No attempt will be made to review extensively the implication of cmc values on detergency. Splendid review papers by Preston (25) and Goette (4) should be studied for their coverage and pertinence.

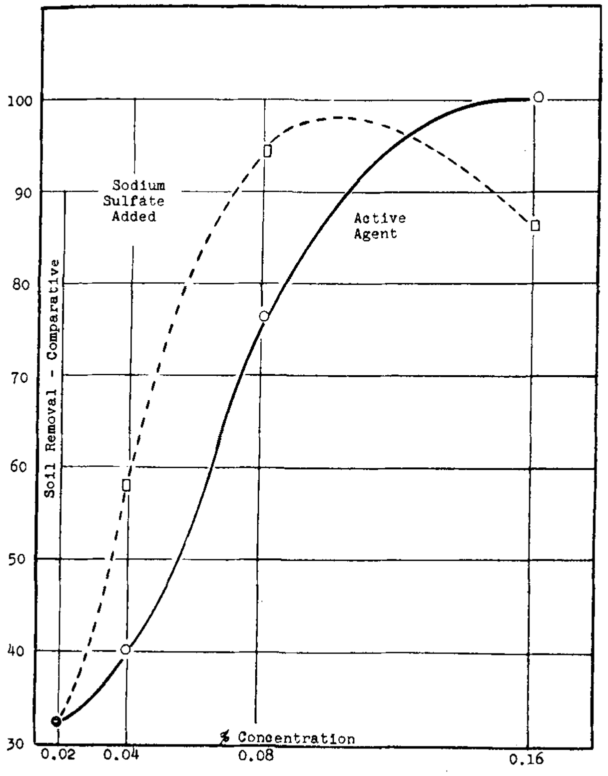
Figure 1 from Preston presents the correlation of cmc measurements by several methods, showing its relevance to the optimum detergency range. Goette acknowledges the pertinence of cmc values to detergency and correctly concludes that cmc values, though interesting, are indicators of only one phenomenon while detergency is the sum of a variety of phenomena, including electrostatic forces, interfacial potentials, and ion activities of both surfactants and builder electrolytes.

One of the outstanding facts concerning cmc values is that the most effective surfactants generally have the lowest cmc while having longer, optimum hydrophobe structure. Consequently a comparison of surfactants can be made on this basis, but of even greater importance perhaps is the measurement of the effect of builder electrolytes upon surfactant cmc. These generally lower the initial cmc remarkably.

While the effect upon cmc of builders is not discussed, Harris' data (6) in Figure 5 shows that lower amounts of surfactant are required to produce a given level of cleaning when builders are used. Table I shows the effect of added electrolyte upon the surface or interfacial tensions of surfactants by added electrolyte, demonstrating the increased effectiveness of the surfactant-builder mixtures. The improvement in wetting time by added sodium sulfate is shown in Figure 6. That the cation has marked effect upon surfactancy (wetting times) is shown in Figure 7. All of the foregoing examples demonstrate the implied effect upon cmc and upon surfactancy by combining electrolyte with surfactant.

Table II demonstrates the effectiveness of added electrolytes upon reducing the critical concentration of sodium laurate. Similar effects can be attained with other surfactants and other builders.

That added solubilized solvents lower cmc (increas-



Active Agent - 100% DDBSS

Sodium Sulfate Added - Same concentration of 100% DDBSS plus 40% Sodium Sulfate

FIG. 5. Effect of sodium sulfate upon detergency of dodecyl benzene sodium sulfonate (6).

TABLE I

Surface-Active Agents—Electrolyte Compositions

Anionic

Surface and Interfacial Tension

Agent and electrolyte	Conc.	Effect of added electrolyte	Author ref.
(1) Sodium cetyl sulfate	0.0001M	ST reduced by	
NaCl	0.02M	24.6 dynes/cm.	
HCl	0.02M	25.2 dynes/cm.	18
NaOH	0.02M	23.4 dynes/cm.	
(2) Sodium dodecyl sulfate	0.0008M		
NaCl	1%	1/9 active to produce same IFT	24
(3) Sodium dodecyl sulfate	0.0025M		
NaCl	0.2%	1/2 active to produce same ST	24
(4) Sodium dodecyl sulfate	0.004M		
$CaCl_2$	0.00045%	1/2 active to produce same IFT	24
(5) Sodium dodecyl sulfate	0.0037M		
$CaCl_2$	0.0006%	1/2 active to produce same ST	24
(6) Igepon T	0.005%		
[$C_{17}H_{33}CON(CH_3)C_2H_4SO_3Na$]	....	IFT reduced from 6.25 to 1 dyne/cm.	27
NaCl	0.32N		
$CaCl_2$	0.003N		
$LaCl_3$	0.00005N		
(7) Sodium oleate	....		
NaCl	0.15N	IFT reduced 7.2 dynes/cm.	
$CaCl_2$	0.0015N	IFT increased 2.45 dynes/cm.	4
(8) Sodium tridecane-7-sulfonate	0.00227M		
	(0.0687%)	1/6 active to produce same ST	3
NaCl	0.13N		
KCl	0.1N		
$MgCl_2$	0.01N		
$CaCl_2$	0.01N		
(9) Diamyl sodium sulfo-succinate	0.1–1%	ST or IFT reduced to that of pure material	2
(Aerosol AY)			
NaCl	0.08%–0.8%		
$MgCl_2$	0.033 –0.33		
$CaCl_2$	0.033 –0.33		

ing potential surfactancy) is demonstrated by Table III. This table also is a good example of the effect of chain length upon cmc: the greater the surfactant action, the lower the cmc.

Many other excellent examples of the relationship between cmc and surfactancy could be chosen from the literature, but the foregoing suffice to indicate the relative importance of cmc to the detergent function.

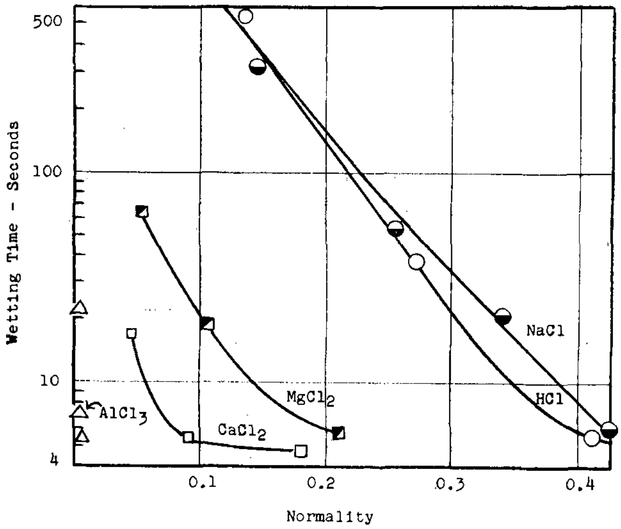


FIG. 6. Canvas disk wetting times with dodecyl benzene sodium sulfonate (6).

Measurement of cmc is a fairly fundamental approach to the problem of surfactancy and the principles evolved are valuable in predicting the course of practical detergency. However, in cmc determination, the formation of micelles is an indication of even more fundamental changes which occur in surfactant solutions. In this respect it may be likened to foaming, solubilization, deflocculation, and suspending action, all of which are complexes of more fundamental activities not yet fully separated and quantitatively measured. It is now no more a substitute for controlled bench-scale detergency tests than the latter are for practical evaluation under replicated, controlled conditions of actual usage.

TABLE II

Effect on cmc of Added Electrolyte (23)
(Orange OT Solubilization Method with Sodium Laurate)

Salt	Salt Molarity	cmc Molarity	% Decrease in cmc
NaCl	0	0.0237	....
	0.0218	1.82	23
	6.9	1.15	51
Na_2CO_3	0 00757	1.82	23
	0.0509	1.26	47
	6.45	1.08	55
$Na_4P_2O_7$	0.00181	2.17	8
	0.0204	1.22	48
	3.15	0.942	60

Principles Governing Micelle Formation

No attempt has heretofore been made at a concise and comprehensive collection of the principles governing micelle formation though Klevens (14) has developed many of them and has discussed them at length.

On the basis that lowered cmc values indicate surfactant effectiveness at lowered concentration levels, the following summary concisely outlines the working principles of micelle formation for ease of utilization.

TABLE III

Effect of Benzene Upon cmc (12)

	Mols per liter		% Decrease in cmc
	No benzene	Benzene	
K soaps			
C_{10}	0.100	0.093	7
C_{12}	0.024	0.020	13
C_{14}	0.0063	0.0051	19
Na alkyl sulfonate			
C_{10}	0.038	0.034	10
C_{12}	0.0092(35.5°C.)	0.0075	19
C_{14}	0.0025(42.5°C.)	0.0018	28

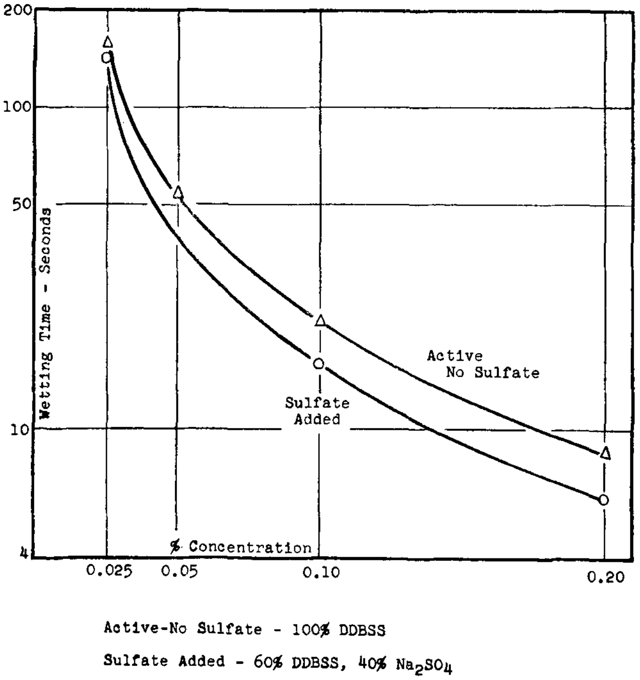


FIG. 7. Canvas disk wetting time at 2.27×10^{-3} molal sodium tridecane-7-sulfate vs. concentration of salt or acid added, at 43.1-46.17°C. (4).

1. Increase in temperature generally increases cmc.
2. cmc is reduced by added electrolyte.
3. cmc is reduced more by added polar than by non-polar solvents.
4. Assuming that quaternary and anionic surfactants act similarly, addition of monohydric alcohols decrease cmc as the chain length of the alcohol is increased.
5. Mixtures of soaps have cmc values intermediate between those of the constituents. The greatest change in cmc results from the addition of the least soluble soap, or expressed differently, soaps with the least tendency to aggregate exert an electrolyte effect upon the other soap.
6. The log of the cmc of anionic soap is linearly dependent upon the log of the cation concentration of the added salt. Electrolyte anions have no influence on the aggregation of anionic soaps (11).
7. Mixtures of the two surfactants of the same cmc but of differing structure produce no observable change in the cmc (10).
8. Influence of cation valence follows the Schulze-Hardy rule: the higher the valency, the less of the cation required to reduce cmc (17, 24).
9. cmc is essentially independent of the nature of the non-colloidal electrolyte ion and is a function primarily of the length of the surface-active ion (14). All straight-chain saturated surfactants of equal ion length have approximately the same cmc.
10. For each decrease in chain length of the surface active ion by one carbon, the cmc will be doubled. When the hydrophilic group (SO_4) is in the middle of the carbon chain, an increase of one carbon atom at the end of each chain does not exhibit the four-fold decrease in cmc expected.
11. Increase in length by a single alkyl group increases cmc when the SO_4 group is moved from the terminal position.
12. Sustitution of a small group in the region of the hydrophilic portion of the molecule effects only a small increase in cmc.
13. Unsaturation in soaps causes a small, but definite increase in cmc. It should be noted that the marked differences in solubility between saturated and unsaturated soaps do not carry over to the formation of micelles.
14. Substitution of polar groups for hydrogen in the alkyl chain results in marked solubility increase and much higher cmc values.
15. For surfactants with polyoxyethylene (POE) chains, cmc increases with increase in POE chain lengths. Surfactants already containing long POE chain lengths will exhibit essentially no changes in cmc with increased POE content. Longer hydrocarbon lengths for the same POE length will show decreased cmc.

Summary

The measurement of critical micelle concentration is discussed from the viewpoint of practical detergent application. Micelles are briefly characterized, and methods for measurement are discussed. The difficulties of measuring nonionic surfactant critical concentrations is indicated, and several applicable methods are described. The practical detergent applications of critical micelle concentration (cmc), as affected by electrolyte builder combinations, are illustrated. A concise summary of the principles governing micelle formation has been developed.

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