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REPORTING EXPERIMENTAL DATA DEALING WITH CRITICAL MICELLIZATION CONCENTRATIONS (c.m.c's) OF AQUEOUS SURFACTANT SYSTEMS

Prepared for publication by
K. J. MYSELS

General Atomic Co., San Diego,
USA

P. MUJERJEE
University of Wisconsin, USA

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Prepared for publication by K. J. Mysels and P. Mukerjee on behalf of Commission I.6 (see Note a).

The IUPAC Manual of Symbols and Terminology makes the following statements about micelles and c.m.c.'s [Appendix II, Part I, 1.6 (see Note b)].

Surfactants in solution are often association colloids, that is, they tend to form *micelles*, meaning aggregates of colloidal dimensions existing in equilibrium with the molecules or ions from which they are formed.

There is a relatively small range of concentrations separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactant forms micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the *critical micellization concentration* (critical micelle concentration), symbol c_m, abbreviation c.m.c. As values obtained using different properties are not quite identical, the method by which the c.m.c. is determined should be clearly stated.

C.m.c. data are determined by a variety of methods and are used in a wide range of areas and specialties. Intercomparison, compilation, and evaluation of results are, therefore, of great importance and require high standards of reporting in the primary literature. This paper suggests criteria for the presentation of experimentally determined c.m.c. values and offers some caveats about the meaning and significance of the data. Attention paid to the considerations here presented should not only help in obtaining significant and reliable c.m.c. data, but also improve their comparability and facilitate their evaluation.

A listing of some 70 methods of determining c.m.c.'s encountered in the literature up to 1966 has appeared recently (see Note c). Although additional methods such as those based on NMR have been developed since that time, there seems to be no need for a further review, nor does it seem necessary to discuss here the reasons for systematic differences between some of the methods, which are described in the same reference.

It may be worth noting, however, that a return to the early definition of the c.m.c. as the concentration at which there is the first perceptible appearance of micelles (as shown by the beginning of a deviation from behavior attributable to nonmicellar species) is not compatible with the above definition and is strongly discouraged. The value of the c.m.c.,

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Note a.   At the time of the approval of this document (1977), the membership of the Commission was: *Chairman:* Dr. K. J. Mysels (USA); *Vice-Chairman:* Prof. R. Haul (GFR); *Secretary:* Prof. J. Lyklema (Netherlands); *Titular Members:* Prof. R. L. Burwell (USA), Prof. R. Hansen (USA), Dr. V. B. Kazansky (USSR), Prof. C. Kemball (UK), Prof. M. W. Roberts (UK); *Associate Members:* Prof. R. M. Barrer (UK), Prof. G. Ertl (GFR), Prof. J. Haber (Poland), Prof. P. Mukerjee (USA), Dr. E. Terminassian-Saraga (France), Dr. I. I. Tretiakov (USSR), Dr. H. van Olphen (USA), Prof. E. Wolfram (Hungary); *National Representatives:* Prof. D. H. Everett (UK), Dr. K. Morikawa (Japan), Prof. W. Schirmer (DDR).
Correspondence Address: Prof. J. Lyklema, Lab. for Physical and Colloid Chemistry, State Agricultural University, De Dreijen 6, 6703 BC Wageningen, The Netherlands.

Note b.   Published in *Pure Appl. Chem.*, Vol. 31, No. 4 (1972), pp. 577-638.

Note c.   Mukerjee, P., and K. J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems,* NSRDS-NBS-36; Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. USA, 1971. Now available from National Technical Information Center, 5285 Port Royal Rd., Springfield, VA 22161, $9.50.

by this early definition, is very dependent on the sensitivity of the method used. In
addition this early definition is inappropriate for extrapolating properties of micelles
to "infinite dilution of micelles," which the IUPAC definition allows.

1. GENERAL

The following principles are basic to the presentation of data:

(a) The work should be described in sufficient detail as regards equipment, conditions,
     and procedure to allow the results to be reproduced and the quality of the work to
     be appraised.

(b) The results should be presented in a form that will permit them to be reworked by
     others to a reasonable extent.

The discussion below does not deal with all possible systems and methods but presents only
points of general importance.

2. EXISTENCE OF A c.m.c.

The existence of a c.m.c. is reflected in a change in the concentration dependence of some
property of the solution over a narrow range. The reverse is, however, not necessarily
true, and real or apparent changes in such dependence need not correspond to a c.m.c. Hence
it is important that there be evidence that indeed below the c.m.c. region the solution is
mainly monomeric whereas above the c.m.c. the number of properly defined micelles increases
rapidly with concentration. Such evidence may be provided directly by the measurement
itself, as in light scattering where the micellar weight is determined simultaneously, or
indirectly from the structure of the surfactant and previous experience as for a long
chain amphipathic compound in aqueous media. For other cases such evidence should be
explicitly presented.

The definition of the c.m.c. implies in particular that for a single surfactant or aggre-
gating species there can be only one c.m.c. A transition of the structure of micelles
above the c.m.c., even though distinct, should not be designated as a second c.m.c.

An essential part of the definition of the c.m.c. is that the transition occurs over a
relatively small range of concentration. It is only then that the c.m.c. can be defined
with some accuracy and only then that the c.m.c. value can be used to decide whether a
solution of a given concentration will be mainly micellar or mainly monomeric. If the
transition range is broad, then a specific value within it may still be determined by any
of a number of procedures, but the concordance between the values obtained by different
methods and by different investigators becomes poor and the difference between the pro-
perties of the solution below and above the value obtained less clear. In other words,
the "critical" part of the c.m.c. gets lost, the clear indication of solution composition
above and below the c.m.c. is not obtained, and what is more serious, a misleading des-
cription of the system may be given.

When only one surfactant is present, "small range" corresponds, in line with the laws
of chemical equilibrium, to relatively "large" micelles. Though the terms remain some-
what arbitrary, in this context "small range" would correspond to less than about 20%
of the c.m.c. and "large" to more than 20 monomers in the micelle. Thus, in systems
showing the "small range," when a micelle with, for example, an average degree of aggre-
gation of 50 become detectable, smaller micelles containing less than 20 or 30 monomers
are not present to a significant extent although all the aggregates are the result of
stepwise self-association. In many cases, although this is not essential, larger micelles
containing more than, say, 70 monomers will also be absent. There are other systems
in which self-association of solutes also occurs by the stepwise association of monomers
to oligomers and multimers, but in such a manner that an average degree of aggregation
of 20 or more will correspond to a wide distribution of aggregate sizes and to the presence
of considerable amounts of smaller aggregates. Such systems may contain micelles but do
not show a "small concentration range" having the meaning and significance normally attached
to c.m.c. values defined above. Though it may be useful to extend the term micelle to such
smaller aggregates, it does seem meaningful to extend the c.m.c. concept to systems in which
the range is much wider than stated. Thus, systems not showing the "narrow range" should
not be assigned c.m.c.'s.

The "relatively small range of concentrations" for the transition corresponds to a relatively
sharp change of the slope on a plot of a measured property vs. concentration. It happens,
however, that this sharpness becomes obscured by the curvature of the lines on both sides
of the c.m.c. It is then often useful to plot $\Delta X/\Delta c$ vs. the average concentration c. Here
Δ indicates the difference between two neighboring experimental points and X a property of
the solution which is roughly additive with respect to monomers and to micelles and increases
(or decreases) with their concentrations. Examples of X are the conductivity of the

solution, or its density or its refractive index. Quantities Y, averaged over one or more species such as molar conductivity or NMR line shift, can be transformed into the additive type by multiplying by c. Thus $\Delta X/\Delta c = \Delta(Yc)/\Delta c$. The sharpness of the transition is indicated by the steepness of that part of the curve that connects the $\Delta X/\Delta c$ plots of the mainly monomeric and the mainly micellar states.

In the case of mixtures of surfactants which form mixed micelles, the situation is much more complicated and the "small range" can also become large because the composition of the micelles changes with total concentration. This situation requires a particularly careful description of the criteria used and an appreciation of the fact that although only large micelles may form, the "micellization concentration" may become an ill-defined range instead of a "critical" one. This is especially so when the components of the mixture have by themselves widely differing c.m.c.'s. Here plots of the $\Delta X/\Delta c$ type can be very useful in indicating the onset of micelle formation.

Listed below are some phenomena unrelated to a c.m.c. which may cause marked changes in the concentration dependence of some property:

A basic surfactant reacts with all the carbon dioxide in the distilled water solvent, or a soap with all the ions responsible for any hardness of water.

The color of an indicator changes when an acid surfactant reaches a concentration giving a suitable pH.

The surfactant, or its association product with an impurity, reach a solubility limit.

The concentration of dimers in a monomer-dimer equilibrium changes as a function of total concentration.

A property varies roughly linearly with concentration and the logarithm of its value is plotted against concentration in the region in which the value of this property is unity. Figure 1 shows a related example for an absorbing system obeying Beer's law. Experimental uncertainties and lack of data points in the transition region can further increase the apparent sharpness of the change of slope.
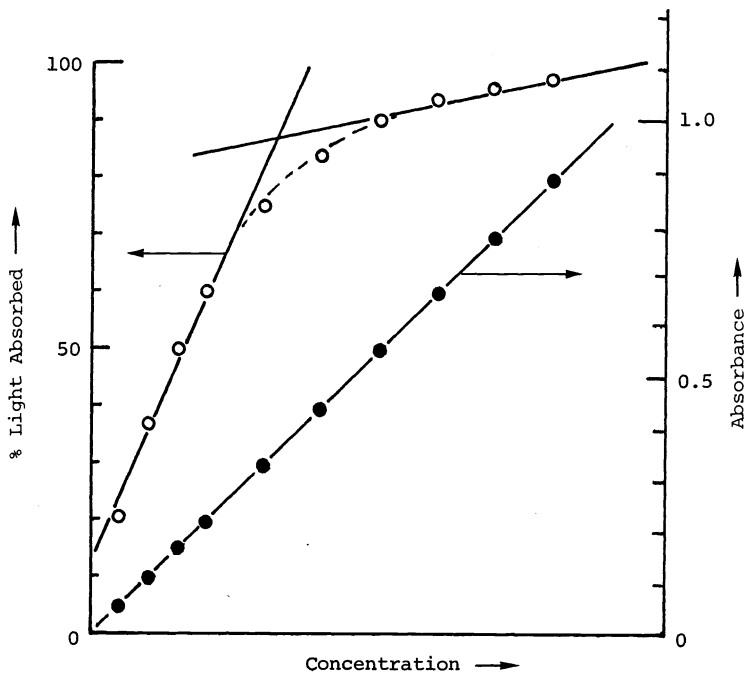

Fig. 1. Same optical data for a compound obeying Beer's law, plotted as % light absorbed and as absorbance. The former could suggest a fictitious c.m.c.

It should also be noted that all directly measurable equilibrium properties of a solution must be continuous functions of the concentration. Their derivatives with respect to concentration may show large changes over a narrow concentration range which may be mistaken for a discontinuity. Any report of discontinuity should therefore be regarded with utmost suspicion.

3. MATERIALS

An important characteristic of the c.m.c. of most surfactants is that it may be sensitive to some impurities and not to others, and that the sensitivity can depend greatly on the surfactant and on the method of determination. Thus the presence of hydrophilic impurities such as sugar generally has little effect whereas that of oleophilic ones such as dodecanol tends to lower the c.m.c., the determining factor being the partition of the impurities between micelle and solvent. The surface tension method seems to be very sensitive to traces of surface active impurities whereas conductivity methods are much less so. Salts of weak acids are sensitive to carbon dioxide in the system and to solution pH, and may form products of hydrolysis that are surface active, whereas salts of strong acid or non-ionics are much less affected by these factors. Hence the possible presence of impurities likely to affect the results in the particular system and the particular method used must receive special attention both in the procedure employed and in the description given.

The c.m.c. should not normally be used as a criterion of identity or purity because of the difficulties of determining it accurately, its low sensitivity to some impurities, and the relatively narrow range in which the c.m.c.'s of many surfactants lie. On the other hand, any significant difference between an observed c.m.c. and that reliably reported (see Ref. 1) is a good reason to doubt the purity or identity of a compound.

Publication of c.m.c. values of systems which contain substantial and unspecified fractions of impurities is undesirable. In particular, the value of data for weak acids, for which the influence of carbonic acid from air, water and reagents is not specified or kept to a minimum, is highly questionable. Needless to say, the above is not intended to discourage the study of well characterized mixed systems or of the effect of known additives upon the c.m.c.

4. APPARATUS AND METHODS

Relative but precise measurements of a property of the solution often suffice for the determination of a c.m.c. This should be kept in mind when describing the instrumental method. In particular, the degree of linearity of instrumental response should be mentioned. Of course, high accuracy is desirable in any published data and should be documented if achieved.

If commercial apparatus is used, it is not sufficient to describe it by a commercial trade name. Rather, its pertinent nature and characteristics must be given either directly or by reference to the scientific literature. It should be remembered that the manufacturer has the right to change specifications without changing names and has no obligation to supply, and continue to supply indefinitely, information about his product.

Concentration changes have to be measured precisely to obtain the concentration dependence whereas the absolute concentration has to be known accurately for the c.m.c. itself. Since c.m.c. values are seldom accurate to better than 0.1%, it is the avoidance of gross errors such as overlooking the presence of water of crystallization that is most important in this respect. Thus final sample conditioning, the molecular weight used, and the method of preparing the solution should be reported, and attention should be paid to a clear statement of units used.

The temperature (or its limits) should be stated explicitly. In some cases, for example with nonionic surfactants, particularly when close to their cloud points, special precautions to assure uniformity and constancy of temperature during measurements are required and should be reported.

5. REPORTING OF RESULTS

There is no substitute for a numerical value given by the author as his best summary of the results. Graphical presentation of c.m.c. values as a function of some variable is not a substitute unless the precision of the c.m.c. is very low. A graphical summary always places a considerable burden on the reader interested in a numerical value. A graph of the variation with concentration of the property leading to the c.m.c. is not a good substitute either, but such a graph can be a great help in judging the value of the numerical result quoted, in addition to being often of intrinsic interest. It is recognized, however, that when more than few c.m.c.'s are reported, it is not always practical to document them all in this way.

The report should include an indication of the reproducibility estimated by the author, specifying the number and the extent of independence of the experiments; e.g., whether starting with different raw materials in the preparation of the sample at one extreme, or making separate dilutions from the same stock solution at the other.

Since the c.m.c. is obtained by extrapolation of two, generally linear, trends from above and from below the c.m.c., the range used in the extrapolation should be reported either in words or in a figure. In precise determinations, any points within the transition range have to be disregarded in the determination of these trends, and therefore, this transition range should also be indicated.