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Critical Micelle Concentrations of Aqueous Surfactant Systems

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Critical micelle concentrations (CMC's), have been collected, organized and evaluated. The literature has been scanned for numerical values from 1926 up to and including 1966. In addition, over 800 values, hitherto available only in graphical form or implied in experimental data, have been extracted from the publications and are included. Close to 5,000 entries, based on 333 references, dealing with 720 compounds are tabulated in the main tables. Whenever available, the temperature, any additives present, the method of determination and the literature source are given for each CMC value and an indication of the apparent quality of the preparation and method used are included. A shorter table gives selected values which are believed to be particularly reliable, including highly accurate ones. Among these, concordant values from at least two independent laboratories are emphasized.

Included in the Introduction is a general discussion of the importance and significance of CMC values and of methods for their determination, as well as a summary of the procedures used in the collection, evaluation and presentation of these values in the present work. Extensive indexes are provided.

Key words: Association colloid; bibliography; CMC; colloid; colloidal electrolyte; critical concentration; critical micelle concentration; detergent; hydrophobic bonding; Krafft point; long chain compounds; micelle; paraffin chain salts; selected values; soap; solubilization; standard values; surface active agents; surface chemistry; surface tension; surfactant.

1. Introduction

Critical micelle concentrations are here to stay! This conclusion is evident from figures 1 to 3 which are based on the literature used in this work. They show a continuing growth since the middle thirties in the number of articles appearing each year which contribute new values and in the number of new values reported. The number of new values per article seems to have passed its peak, which suggests more careful and critical work in recent years.

The reason for this growth is that a critical micelle concentration (CMC) is probably the simplest means of characterizing the colloid and surface behavior of a surfactant solute, which in turn determines its industrial usefulness and biological activity, and gives a measure of the structurally interesting solute-solvent and solute-solute interactions. However, these published CMC values are widely scattered through the literature—we have consulted 87 different publications—and vary greatly in quality from clearly erroneous data to highly accurate values.

Furthermore, some of the existing values are clearly tabulated, but others—often the best ones—are hidden in graphs, or even in tabulations of some measured property such as conductivity. These require considerable effort and judgment to retrieve. Frequently, the quality of the work cannot be judged without consultation of several references and intercomparison with other pertinent publications. Hence, much of the literature is not now readily accessible or useful to those interested in learning what has been established thus far.

The primary purpose of this publication is to provide a list of values in which the user can place high confidence. In the process of obtaining these, we had to make a survey, as complete as possible, of all available values. To present the results of this survey so as to make both the literature and the results contained therein readily available became, therefore, a secondary objective. Perhaps the best evidence for the usefulness of this effort is that nearly two-thirds of the best data reported herein were not previously directly available in the literature but required at least some, and often quite extensive, interpretation of a publication or individual correspondence.

The book itself is divided into four parts:

(1) The Table of Recommended and Selected Values lists the values we believe to be most reliable. They contain further guides to the quality of the data.

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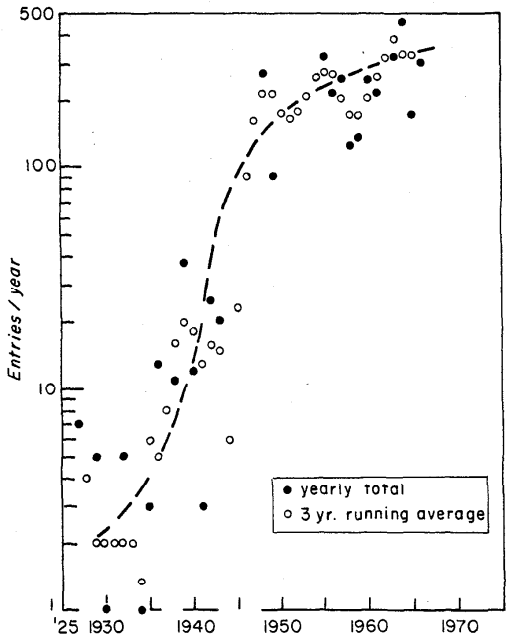

FIGURE 1. *Number of entries for the complete tables originating within each year from 1927 to 1966.*

There are no entries in 1928, 1931, 1933, 1934, 1937 and 1945.

(2) The Complete Table contains all values found which were published through 1966.

(3) Several indexes and lists, particularly the compound indexes, should permit the reader to find any desired compound or its closest analogs, give him the meaning of any abbreviation or symbol, and also guide him to the pertinent literature.

(4) The Introduction discusses the thoughts that went into the collection, evaluation, and presentation of the data. A glance at "How to Use These Tables" may be helpful before consulting them.

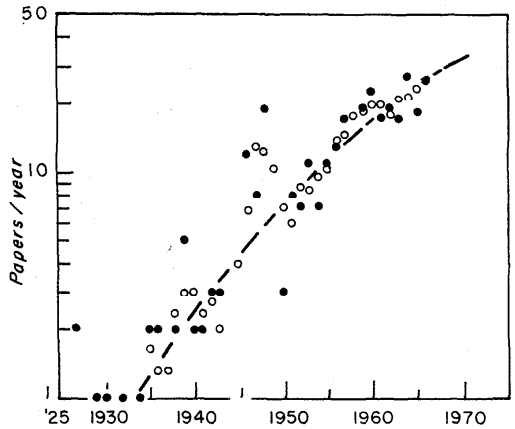

FIGURE 2. *Number of papers containing at least one entry for the complete tables originating within a given year.*

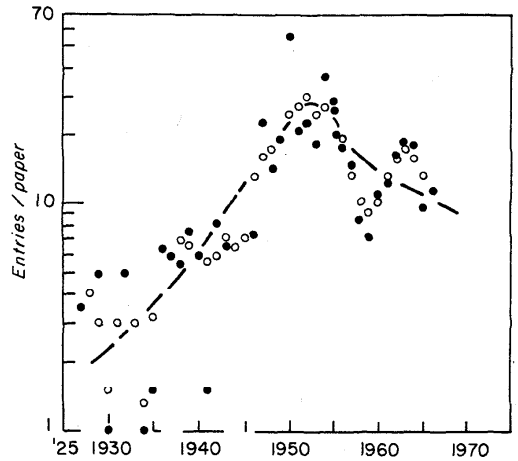

FIGURE 3. *Average number of entries per paper containing at least one entry within a given year and within a three year period.*

The largest number of entries from a single paper was 167, from reference 55004.

We hope that this work will make us more friends than enemies. We tried to be objective in the evaluation of the data, but some errors and personal prejudices are unavoidable. Our evaluation procedure of the individual data is described in the introduction, which contains also general considerations about the validity and significance of the various methods of determination.

We are grateful to many who have helped us in this work. Close to a hundred authors have responded to our request for reprints and many have provided additional comments, data, and interpretations. Dr. Edward L. Brady was most helpful in getting us started properly in the task of handling this multitude of data. Dr. H. J. White's patience and cooperation are greatly appreciated. The extensive computer handling of the data was made possible by the free availability of the data processing facilities of the R. J. Reynolds Tobacco Co., and the programming skill and understanding of Mr. Bill Donovan. Several secretaries have been involved in the careful verification of the hundreds of thousands of bits of information recorded. Mrs. Jerry Wilson and Miss Judy Tate were particularly involved in the final stages. The work leading to this publication was begun in 1964 at the University of Southern California under contract with the National Bureau of Standards and continued there until September 1966 when the authors transferred to their present connections with the University of Wisconsin, where the support of the National Bureau of Standards continued, and the R. J.

Reynolds Tobacco Co. Clearly, the resources of these three institutions made the completion of our work possible.

2. How to Use the Tables

This section presents a brief guide to the admittedly complicated arrangement of the tables. Space and computer requirements dictated much of this complexity; some is inherent in the dissimilarity of the compounds and the variety of conditions used for CMC determinations. The guide is arranged to answer a series of questions which may be raised by readers.

How do I find the compound I am interested in? In the tables the compounds are arranged in numerical order by arbitrary "Compound Numbers." To find this number you must go through the "Compound Index" in which the listed compounds are arranged by structure. There are five parts to this index (plus an alphabetical one for commercial names) and in each the compounds are listed according to different structural properties. These arrangements are described on the first page of the compound index (p. 23).

What can I do if my compound is not listed? The indexes will lead you to the most closely related compounds that are listed. These should permit you to make a good guess by interpolation and extrapolation.

How do I learn about the effect of an additive? The names of additives are abbreviated (if the abbreviation is not clear, its meaning can be found in the list on p. 222). Surfactant additives are indicated by their "Compound Number." For each compound, CMC values in the presence of additives are listed after the simple (surfactant-water) system in alphabetical order of the abbreviations. This is followed by systems with two additives and then by those with three additives.

What if the additive is not listed with my compound? The additive index shows all the compounds reported for any additive. You may find some useful analogies in this way.

What is the effect of temperature? Within each system (compound-additive(s)) the values are arranged by increasing temperature. By checking the author, or better the reference column, you can locate groups of values that were obtained specifically to show the effect of temperature (which is often small).

Which are the "good" CMC values? The shorter tables beginning on page 51 contain the "Selected" and "Recommended" values (15% of all reported values). Those that carry a "1" in the last column have been independently confirmed and should be highly reliable (to 1.5%, keeping in mind that different methods can give significantly different values—cf. p. 11). Those marked "2" are of the same apparent quality but lack confirmation. Among those marked "D" for each system, there is probably one that is as good as those of the preceding categories, but we do not know which. The many marked "3" do not seem to be in the same class but should be good to 10 percent.

What do I find in the long tables? These tables beginning on page 66 contain all the "Recommended and Selected" values plus all the others that we have located. In a number of cases, indicated by "R" in the last column, we make references to the literature where additional data or calculated values may be found or to warn the reader that the values are duplicates of those already listed or are in error. The bulk of the values carry an "L" in the last column. These may be useful and some may be excellent but we could not "recommend" or "select" them for a variety of reasons. Some clue to these reasons may be found in the "quality" column.

What is the "quality" column? In this column the first letter refers to the material and the second to the measurement. The meaning of the letters may be found on page 6. In general the quality decreases in alphabetical order. It represents our opinion after a careful study of the reference.

Are there more data in the literature? Our search does not cover anything published in 1967 or later (including the 1964 Congress of Surface Activity which did not appear in print until 1968). There are also older references that we may have overlooked. All the references within this field that we have scanned are listed in the literature index starting on page 213 whether they have yielded any entries or not. We would like to be informed of overlooked articles. Some of the literature scanned does contain data which, if properly interpreted, could lead to a CMC value which is not included. We have made such interpretations in many hundreds of cases, but not always. However, if a CMC value was mentioned as such in the article, we have tried to include it in all cases.

What are those various "methods"? The "method" column contains generally an abbreviation of the

method by which the CMC value was obtained. These methods are discussed briefly (and their abbreviations given) on pages 8 to 11. The "methods index" lists the references which have used each. These references should be consulted for details.

Occasionally the methods column contains information about the literature or a cross-reference. This is only the case when the entry does not give a CMC value.

In what units are the CMC's? We have followed the references except for order of magnitude conversions (e.g., from millimoles to moles) and as a result have a large number of units. The meaning of the abbreviations is given on page 222 and in the footnote to the table. For noncommercial compounds, for which a molecular weight is likely to have meaning, we have added a value in moles (per liter or kg of solution or kg of solvent) when the corresponding weight concentration of the compound was given. This was done by the computer on the basis of the molecular weight listed for the compound which in turn was also obtained by the computer from a structural or empirical formula of the compound. The value is printed by itself on a separate line below the value given by the author and is characterized by "M" in the "source" column.

What units are used for additives? The same units and symbols as for CMC's plus a number of others, including such peculiar ones as pH, again following the authors. In addition, we have used the additive columns to record certain special conditions such as pressure. The meaning of the abbreviations is listed on page 222. For additives we have not made any conversions to mole units.

What compound nomenclature is used? We have generally followed the first author whom we encountered dealing with the particular compound in the hope that this will also be the most common and understandable name. In case of ambiguity or some exotic names, we have added an alternative name or a formula in parentheses.

Are there any values for solvents other than water? If the solvent is a mixed one including water, the other components have been considered as additives. Nonaqueous systems have not been included for reasons discussed on page 18 with the exception of D_2O which is treated as an additive at 100 mole percent concentration!

What is the meaning of "source"? This column serves to indicate in what way the pertinent CMC value was obtained by us. The meaning of the abbreviations is listed on page 222. In some cases the reader can check our listing directly or after carefully reading a graph or replotting some numerical data. In a few cases, however, our listing is based not only on what appears in the article but on correspondence or conversation with the authors. In this case an L in the source column is given. We have not included, however, values made available to us privately which did not have a basis in the published literature.

Where do these CMC's come from? The exact reference may be found in the Reference index starting on page 213 through the number in the "reference" column of each entry. However, much information can be obtained from this number itself since the first two digits give the year of publication and from the "authors" column which carries the first four letters of the name of the author or two of the authors of that publication. Particularly for those familiar with the field, this should often permit identification of the reference.

Are the numbers of digits really significant? Not in the great majority of entries. We have again followed the authors for the sake of the record and it is clear that most authors paid no attention whatsoever to the rules pertaining to significant figures. A better idea of the precision of the values is given by our "quality" rating of the method (second letter). See page 6 for the approximate meaning of these letters. When the value quoted is obtained by ourselves from published graphs, etc., the significant figures refer to how well these graphs could be read or interpreted without digging further into the uncertainties of the experiment.

3. Usefulness of CMC Value

The expression critical micelle concentration (CMC), as will be discussed later, is slightly misleading because of the use of the singular form of the noun "concentration." The formation of micelles from the constituent monomers involves a rapid, dynamic, association-dissociation equilibrium. Experimentally, it is found, in accord with the expectations from such equilibria, that micelles are undetectable in dilute solutions of the monomers, and become detectable over a narrow range of concentrations as the total concentration of solute is increased, above which nearly all additional solute material forms micelles. The concentration at which the micelles become first detectable depends on the sensitivity of the experimental probe used. The concentration range over which

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