MONTANA STATE UNIVERSITY

Aspects of surfactant micellization
by Ahmad Befroeyeh Rezvani

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University
© Copyright by Ahmad Befroeyeh Rezvani (1983)

Abstract:
Many molecules and ions possessing hydrophilic and hydrophobic regions aggregate in solution. Although the resulting micelles have been studied intensively since McBain first postulated their existence in 1913 (16), much remains to be learned about the micellization phenomenon.

The current work concerns two facets of micellization: (1) the ability of micelles to catalyze a number of chemical reactions and (2) the influence of counterion structure on micellar parameters.

Bunton et al. (8) reported that micelles enhance the decarboxylation of 2-cyano-2-phenylacetic acid by a factor as great as 660 and postulated an electrostatic interaction between the micelle surface and the substrate which stabilizes the transition complex. If this is the case, structural changes in the polar heads of the surfactant ions comprising the micellar surface should affect the reaction rate. One problem was to determine the extent catalysis in the decarboxylation reaction is influenced by alterations in the surfactant ion's polar head.

Two samples of 2-cyano-2-phenylacetic acid were used in the investigation. Although both had melting points that agreed closely with literature values, their ultraviolet spectra differed somewhat. In basic solution, the first sample exhibited a broad absorption band in the 2800 A region which decreased with time. The rate of disappearance of the band was inhibited by cationic surfactants. Under similar conditions, the spectrum of the second sample of acid did not possess the broad absorption band. Attempts to follow the decarboxylation in the manner employed by Bunton et al. (8) were fruitless. Further research is required to answer the questions raised.

Menger et al. (11) determined the critical micelle concentrations and aggregation numbers of decyltrimethyl-ammonium micelles in 0.25m solutions of the organic dianions: phthalate, isophthalate and terephthalate. The most symmetrical anion, terephthalate, had the least influence in lowering the critical micelle concentration. The second problem of this research was to determine whether the three benzene tricarboxylate counterions behave similarly. In agreement with Monger's work, we find that the critical micelle concentration is highest when the most symmetrical counterion is employed. Aggregation numbers are little affected by the geometry of the counterion.

ASPECTS OF SURFACTANT MICELLIZATION

by

Ahmad Befroeyeh Rezvani

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

October 1983

APPROVAL

of a thesis submitted by

Ahmad Befroeyeh Rezvani

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Oct. 17, 1983
_____
Date

E. W. Gmarker
_____
Chairperson, Graduate Committee

Approved for the Major Department

Oct. 17, 1983
_____
Date

Edwin H Abbott
_____
Head, Major Department

Approved for the College of Graduate Studies

10-24-83
_____
Date

Michael Malone
_____
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his/her absence, by the Director of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature _Ahmad Keyvani_

Date _10-17/1983_

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

ABSTRACT

Many molecules and ions possessing hydrophilic and hydrophobic regions aggregate in solution. Although the resulting micelles have been studied intensively since McBain first postulated their existence in 1913 (16), much remains to be learned about the micellization phenomenon.

The current work concerns two facets of micellization: (1) the ability of micelles to catalyze a number of chemical reactions and (2) the influence of counterion structure on micellar parameters.

Bunton et al. (8) reported that micelles enhance the decarboxylation of 2-cyano-2-phenylacetic acid by a factor as great as 660 and postulated an electrostatic interaction between the micelle surface and the substrate which stabilizes the transition complex. If this is the case, structural changes in the polar heads of the surfactant ions comprising the micellar surface should affect the reaction rate. One problem was to determine the extent catalysis in the decarboxylation reaction is influenced by alterations in the surfactant ion's polar head.

Two samples of 2-cyano-2-phenylacetic acid were used in the investigation. Although both had melting points that agreed closely with literature values, their ultraviolet spectra differed somewhat. In basic solution, the first sample exhibited a broad absorption band in the 2800 Å region which decreased with time. The rate of disappearance of the band was inhibited by cationic surfactants. Under similar conditions, the spectrum of the second sample of acid did not possess the broad absorption band. Attempts to follow the decarboxylation in the manner employed by Bunton et al. (8) were fruitless. Further research is required to answer the questions raised.

Menger et al. (11) determined the critical micelle concentrations and aggregation numbers of decyltrimethyl-ammonium micelles in 0.25m solutions of the organic dianions: phthalate, isophthalate and terephthalate. The most symmetrical anion, terephthalate, had the least influence in lowering the critical micelle concentration. The second problem of this research was to determine whether the three benzene tricarboxylate counterions behave similarly. In agreement with Menger's work, we find that the critical micelle concentration is highest when the most symmetrical counterion is employed. Aggregation numbers are little affected by the geometry of the counterion.

INTRODUCTION

As their name suggests, surfactants (acronym formed from surface active agents) lower the surface tension of water. Because of this and other special properties, they have many uses, e.g., as cleaners, emulsifiers, corrosion inhibitors, lubricants, bactericides and catalysts.

It is generally accepted that any valid explanation of all facets of surfactant behavior must include micellization as a basis tenet, i.e., the aggregation of monomeric surfactant ions (molecules) to form colloidal particles or micelles. In general, a surfactant ion has a hydrophobic and a hydrophilic part. The decyltrimethylammonium ion, $CH_3(CH_2)_9 N^+(CH_3)_3$ is illustrative. The hydrocarbon tail, $CH_3(CH_2)_9-$, is "water-hating" and the polar head, $-N^+(CH_3)_3$, is "water-loving." Micelle formation is a compromise which permits both parts of the surfactant ion to reside in compatible environments. Hartley (1) succinctly described the situation in stating that the surfactant ions "aggregate with their chains jumbled together and away from the water and their end groups projecting into the surrounding water."

Micelle size increases with the addition of simple electrolyte (2), when the surfactant ion's hydrocarbon tail is lengthened (3), when the counterion (small ion associated

with the surfactant ion in the neutral state) is made more polarizable (4), and when the polar head is made less bulky (5). Light scattering measurements indicate that when concentrations of surfactant and simple electrolyte are low, micelles are roughly spherical with aggregation numbers (number of surfactant ions per micelle) generally in the range of 35 to 150.

Throughout the last two decades there have been numerous studies of the catalysis of various chemical reactions by surfactant micelles. Although the rate enhancement is rarely greater than a factor of 100 (6), it can be much higher. Sodium laurylsulfate, for example, will enhance the Hg (II) - induced aquation of $Co(NH_3)_5Cl^{+2}$ by a factor of 42,000 or more (7). C. A. Bunton, A. Kamego, and M. J. Minch (8) found that the rate of decarboxylation of the 2-cyano-2-phenylacetate ion is catalyzed ca. 660-fold at 25°C by micelles of cetyltrimethylammonium bromide. Presumably, the reaction involves the formation of a carbanion-like transition complex which interacts strongly with the micelle. According to Bunton et al. (8), "Decarboxylations in which a carboxylate ion generates a carbanion-like transition state are strongly catalyzed by cationic micelles. The electrostatic interactions between the cationic micelle and the carboxylate ion assist the incorporation of the latter into the micelle and, of itself, this stabilization of the initial state would result in a

rate reduction unless the transition state, with its delocalized negative charge, interacts more strongly with the micelle than the more localized carboxylate ion and offsets this rate reduction."

If electrostatic interactions between the micellar surface and the carboxylate ion (transition complex) are involved in micellar catalysis, then it follows that structural changes in the polar groups of the surfactant ions should influence the reaction rate. We decided to measure the rates of decarboxylation of 2-cyano-2-phenylacetic acid with a series of surfactants as catalysts. Since the polar head structure was to be changed systematically from one member to the next in at least a part of the series, we expected the strength of the interaction between micelle and transition complex - and therefore the reaction rate - to also change in a regular manner. An ultimate goal of research of this type is to correlate reaction rate with polar head structure. As the Fendlers have stated (6): "The use of micelles in synthetic organic chemistry is to alter the yields and reaction pathways has great potential and is a relatively unexplored area of research which merits attention."

Recent surfactant research at Montana State University has been concerned with the influence of organic counterions on micellar parameters. Anacker and Underwood (9) compared the tendencies of seven n-alkycarboxylates to promote the

formation of decyltrimethylammonium micelles. Although lengthening the alkyl chain beyond two or three carbon atoms lowered the critical micelle concentration (surfactant concentration above which most of any surfactant added to a solution micellizes) and increased the aggregation number, the carboxylates proved not to be as strong promoters of micellization as a number of inorganic counterions. Switching the counterion from formate to heptanoate increased the aggregation number of decyltrimethylammonium micelles from 37 to 48. With the DODTMAB surfactant ion, switching the counterion from iodate to thiocyanate increased the aggregation number from 38 to 8,700 (10). Concentrations of counterions in all solutions were the same, 0.500 molal.

F. M. Menger, D. Y. Williams, A. L. Underwood, and E. W. Anacker (11) studied the effect of counterion geometry on the critical micelle concentrations and aggregation numbers of decyltrimethylammonium micelles. The isomeric counterions involved were phthalate, isophthalate, and terephthalate:
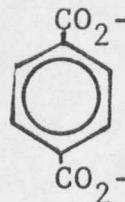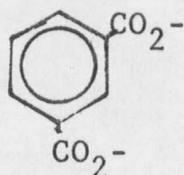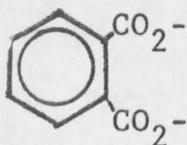
Critical micelle concentrations and aggregation numbers, as determined by light scattering, in solutions 0.25 molal in the counterions are:

Counterion	CMC (mole/kg)	Aggregation No.
Phthalate	0.027	38
Isophthalate	0.025	46
Terephthalate	0.050	30

Menger et al. summarized this study as follows: "We find no evidence that the CMC, aggregation number, and binding of micelles responds sensitively to the geometry of the counterion when polarizability, hydrophobicity, etc., are left relatively constant.... The micelle surface is pictured as having water-filled grooves and fatty patches, being much more disorganized than in the classical Hartley model. Consequently, the micelle surface displays little preference for the disposition of the carboxylates attached to the aromatic ring."

As an extension of the work of Menger et al., we decided to study the effect of isomerization in benzene-tricarboxylate counterions on the micellar parameters of decyltrimethylammonium ions. An additional incentive was the opportunity to work with trivalent counterions. Most counterion work in the past has involved monovalent species. Some unpublished work of Anacker and Underwood with SO_4^{2-}

indicates that this divalent counterion is less effective in promoting micellization than many univalent inorganic ions, Br^- for example. We thought it would be interesting to see if this trend carried over to organic counterions.