

COLLOIDAL
SURFACTANTS
SOME PHYSICOCHEMICAL PROPERTIES

PHYSICAL CHEMISTRY

A Series of Monographs

Edited by

ERNEST M. LOEBL

*Department of Chemistry, Polytechnic Institute of Brooklyn
Brooklyn, New York*

- 1 W. JOST: Diffusion in Solids, Liquids, Gases, 1952
- 2 S. MIZUSHIMA: Structure of Molecules and Internal Rotation, 1954
- 3 H. H. G. JELLINEK: Degradation of Vinyl Polymers, 1955
- 4 M. E. L. MCBAIN and E. HUTCHINSON: Solubilization and Related Phenomena, 1955
- 5 C. H. BAMFORD, A. ELLIOTT, and W. E. HANBY: Synthetic Polypeptides, 1956
- 6 GEORGE J. JANZ: Thermodynamic Properties of Organic Compounds — Estimation Methods, Principles and Practice, revised edition, 1967
- 7 G. K. T. CONN and D. G. AVERY: Infrared Methods, 1960
- 8 C. B. MONK: Electrolytic Dissociation, 1961
- 9 P. LEIGHTON: Photochemistry of Air Pollution, 1961
- 10 P. J. HOLMES: Electrochemistry of Semiconductors, 1962
- 11 H. FUJITA: The Mathematical Theory of Sedimentation Analysis, 1962
- 12 K. SHINODA, T. NAKAGAWA, B. TAMAMUSHI, and T. ISEMURA: Colloidal Surfactants, 1963
- 13 J. E. WOLLRAB: Rotational Spectra and Molecular Structure, 1967
- 14 A. NELSON WRIGHT and C. A. WINKLER: Active Nitrogen, 1968
- 15 R. B. ANDERSON: Experimental Methods in Catalytic Research, 1968

COLLOIDAL SURFACTANTS

SOME PHYSICOCHEMICAL PROPERTIES

By

KOZO SHINODA

*Department of Chemistry
Yokohama National University
Minamiku, Yokohama, Japan*

TOSHIO NAKAGAWA

*Research Laboratories
Shionogi Pharmaceutical Company
Imafuku, Amagasaki-shi, Japan*

BUN-ICHI TAMAMUSHI

*Tokyo Women's
Christian College
Suginamiku, Tokyo, Japan*

TOSHIZO ISEMURA

*Department of Biology
Osaka University
Kitaku, Osaka, Japan*



1 9 6 3

ACADEMIC PRESS • NEW YORK AND LONDON

COPYRIGHT © 1963, BY ACADEMIC PRESS, INC.

ALL RIGHTS RESERVED.

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT
WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS, INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
Berkeley Square House, London W.1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 62-13114

Second Printing, 1969

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE

In almost all branches of the chemical industry, surface active agents have found wide use. The many interrelations with various fields of science have stimulated rapid progress in research on the extremely interesting properties of these substances.

Surface active agents are of great importance in detergency, in the textile industry, and in biological research. This is due to their following distinctive features: (1) moderate maximum concentration of molecularly dispersed species; (2) surface and interfacial depression in very dilute solution, due to the adsorption and orientation of molecules at the interface, (3) micelle formation above a certain concentration, due to the free energy decrease of the system; and (4) solubilization of water-insoluble substances by micelles.

Considerable research work with surface active agents has been carried out in Japan; this work, however, is not well known in other countries because many of the papers were published in Japanese, and even those written in English for the *Bulletin of the Chemical Society of Japan* are not widely read.

For this reason, one of us (K.S.), together with several colleagues, planned to publish a book on this subject. Fortunately, Professor Eric Hutchinson, the Editor of this series, came to Yokohama National University as Fulbright Exchange Lecturer for the academic year of 1959-1960. Professor Hutchinson's stay in Japan provided a rare opportunity for cooperative activity toward this end and we wish to express our sincere gratitude to him for his encouragement and many helpful suggestions.

We are grateful to the Daiichi Pharmaceutical Company for various surface active agents.

B. TAMAMUSHI
T. ISEMURA
T. NAKAGAWA
K. SHINODA

May, 1962

This page intentionally left blank

CONTENTS

PREFACE	v
-------------------	---

CHAPTER ONE. The Formation of Micelles

Kōzō SHINODA

I. An Outline of the Behavior of Surface Active Agents in Solution	1
II. Methods of Measuring the Critical Micelle Concentration	9
III. The Size and Shape of Micelles	16
IV. The Theory of Micelle Formation	25
V. The Effect of Molecular Type on the Critical Micelle Concentration	42
VI. The Effects of Additives and Salts on the Critical Micelle Concentration	58
VII. Surface Activity.	79
VIII. The Formation of Micelles in Non- aqueous Solution	80
References.	88

CHAPTER TWO. Physicochemical Studies in Aqueous Solutions of Non- ionic Surface Active Agents

TOSHIO NAKAGAWA AND Kōzō SHINODA

I. Introduction	97
II. Critical Micelle Concentration	98
III. Micellar Weight.	112
IV. Temperature Dependence of Critical Micelle Concentration and Micellar Weight.	121
V. Clouding	129
VI. Interaction with Other Substances	135
VII. Other Physicochemical Properties.	160
VIII. Purification and Chromatography	163
IX. Analysis	173

References	175
----------------------	-----

CHAPTER THREE. Adsorption

	BUN-ICHI TAMAMUSHI
I. Introduction	179
II. Adsorption at the Solution-Air and So- lution-Oil Interfaces	181
III. Adsorption at the Solution-Mercury Inter- face	203
IV. Adsorption at the Solution-Solid Interface	216
V. Interaction of Paraffin Chain Electrolytes with Colloids	230
References	246

CHAPTER FOUR. Monomolecular Layers

	TOSHIZO ISEMURA
I. Introduction	251
II. General Aspects of Monolayers	252
III. Experimental Techniques	255
IV. Monolayer Studies of Surface Active Agents	259
V. Surface Activity of Protein	270
VI. Surface Activity of Synthetic Polymers	274
VII. Interaction at Interface	281
VIII. Equation of State of Ionized Monolayers	284
References	288

AUTHOR INDEX	291
SUBJECT INDEX	301

COLLOIDAL
SURFACTANTS
SOME PHYSICOCHEMICAL PROPERTIES

This page intentionally left blank

CHAPTER ONE

THE FORMATION OF MICELLES

K Ō Z Ō SHINODA

I. An Outline of the Behavior of Surface Active Agents in Solution

The distinctive features of surface active agents are: (1) their moderate maximum concentration of molecularly dispersed species; (2) surface and interfacial tension depression in very dilute solution, due to the adsorption and orientation of molecules at the interface; (3) micelle formation above a certain concentration, which has been termed the critical micelle concentration (CMC), due to the free energy decrease of the system; and (4) solubilization of water-insoluble substances by micelles.

The great importance of surface active agents in the textile industry, in detergency, biological actions, etc. has resulted from these peculiar properties. The applications of surface active agents have been rapidly increasing, and an understanding of their physicochemical properties is becoming more and more important to scientists in various fields.

Before discussing the dissolution tendency of surface active agents, which are composed of either an ionic or a nonionic hydrophilic group and a hydrocarbon chain, it seems helpful to outline the factors which control the solubility of simple salts and hydrocarbons, respectively, in water.

In the vapor state the calculation of the equilibrium of



is straightforward. From the statistical thermodynamic relation in general chemical equilibrium (1),

$$\frac{N_{\text{Na}^+} N_{\text{Cl}^-}}{V N_{\text{NaCl}}} = \frac{f_{\text{Na}^+} f_{\text{Cl}^-}}{f_{\text{NaCl}}} \exp(-\Delta\chi/kT) \quad (1.2)$$

where N_{NaCl} , N_{Na^+} , and N_{Cl^-} are the mole numbers of NaCl, Na^+ , and Cl^- ions in the vessel; f_{NaCl} , f_{Na^+} , and f_{Cl^-} are the partition functions of NaCl, Na^+ , and Cl^- ; $\Delta\chi$ is the excess energy of a pair of free Na^+ and Cl^- ions at rest over one NaCl molecule at rest in its lowest vibrational state; V is the volume of the vessel; k is the Boltzmann constant; and T is the absolute temperature. The ratio of the partition functions of the

dissociated ions to that of the salt is much larger than 1, and this term contributes to the dissociation. The factor $\exp(-\Delta\chi/kT)$, which is much smaller than 1, restrains the dissociation. In other words, the electrical energy required for the separation of ions decreases the dissociation, and the translational entropy increase due to the separation of ions increases the dissociation.

The mutual potential energy of Na^+ and Cl^- is approximately $\Delta\chi = 8.6 \times 10^{-12}$ ergs/ion pair.

The partition function of these simple particles can be easily calculated assuming that the vibrational partition function is close to 1 at room temperature, which is a reasonable assumption. Substituting these values and expressing the equilibrium concentration C in gram ions (or gram molecules) per liter, the equilibrium constant at 300°K in the gas phase is,

$$K = \frac{C_{\text{Na}^+}C_{\text{Cl}^-}}{C_{\text{NaCl}}} \simeq 10^2 \exp(-\Delta\chi/kT) \approx 10^2 \exp(-210) = 10^{-89} \quad (1.3)$$

Thus, ordinary salt is naturally completely undissociated in the vapor phase. If we regard water merely as a continuous medium (unhydrated) with dielectric constant $D \approx 80$, the energy of separation of the pair of ions would be reduced to roughly $\Delta\chi/D$. We thus obtain in water (1)

$$K_{\text{NaCl}} = \frac{C_{\text{Na}^+}C_{\text{Cl}^-}}{C_{\text{NaCl}}} \simeq 10^2 \exp(-2.6) \simeq 7 \quad (1.4)$$

In the very strong fields near an ion, a saturation effect sets in, which reduces considerably the effective value of D . The correct value of the equilibrium constant must be much less than 7 in the absence of hydration. Nevertheless, the above discussion explains the large dissociation of salts or ionic surface active agents in water. Dissociation is caused by the entropy increase at the expense of the energy required to separate the ions. As the nonelectrical heat of solution of salt in water or in organic solvents is far less than $\Delta\chi$ ($\Delta\chi$ is about 120 kcal/mole), the above discussion is able to explain the large dissociation and solubility of salts in water and the negligible dissociation and solubility in hydrocarbons whose dielectric constants are about 1 or 3.

If we immerse ionic surface active agents, for example sodium dodecyl sulfate, in water, the "gegenion" Na^+ dissolves in water by the same entropy effect. The dissociation of 1:1 electrolytes into separate ions increases the total entropy considerably. After dissolution of the sodium ion, the solid ionic surface active agent carries a negative charge and this electrical repulsion increases the solvency of the dodecyl sulfate ion in water. The so-called "hydrophilic group" in an ionic surface active agent has the property of being readily soluble in water, but the

heat of solution assigned to the hydrophilic group is not necessarily exothermic. It is not the "sympathetic force" (2) of the hydrophilic group, but rather the entropy increase due to dissociation, which enhances the dissolutive tendency of ionic agents. In spite of their great solubility, the heat of solution of many inorganic salts is generally negative.

There is, however, no dissociable group in a nonionic surface active agent. There is some "sympathetic force" between the hydrophilic portion of the molecule and the surrounding water molecules. The oxygen atom in the hydrophilic group of nonionic agents has a relatively large attraction for water molecules, but the increase of solvency due to this portion is small because the ethylene groups in the polyoxyethylene chain cancel the effect. There is also some positive configurational entropy of solution due to the long and large hydrophilic group of the molecule. Both these effects are usually small (3) compared to that of an ionic group, due to dissociation. For this reason, the maximum concentration of molecular dispersion, i.e., the critical micelle concentration, is very much smaller in nonionic surface active agents whose hydrocarbon chain is the same as that of ionic agents. For example, the CMC of sodium dodecyl sulfate is 0.0081 mole/liter, whereas that of dodecyl glucoside is 0.00019 mole/liter (4).

The "antipathy" between the oleophilic portion and the water molecules does not involve an actual repulsive force between the two (2). As the cohesive forces between the water molecules are very strong and the cohesive forces between hydrocarbon-hydrocarbon or hydrocarbon-water are not strong, the separate phase state has a lower energy than the mixed state. Were there no hydrophilic group in the molecule, i.e., in the case of hydrocarbon, the entropy of dilution would have to counterbalance the heat of solution of hydrocarbon. The effect of molecular size, i.e., hydrocarbon chain length on solubility, can be understood by analogy with the regular solution theory developed by Hildebrand (5)

$$\ln a_2 = \ln X_2 + \frac{V_2 \phi_1^2 (\delta_1 - \delta_2)^2}{RT} \quad (1.5)$$

where a_2 is the relative activity of solute and is very close to 1 at saturation if the solubility of component 1 (liquid) in component 2 (liquid) is small; X_2 is the solubility of solute (hydrocarbon) in mole fraction units; V_2 is the molal volume of solute; ϕ_1 is the volume fraction of solvent; and δ_i are the solubility parameters of the components. The second term expresses the contribution of the heat of solution to the solubility. (There are also structural enthalpy and entropy changes in the case of hydrocarbon in water, but they largely cancel out.) When we discuss the solubility of hydrocarbons in a very different solvent, such as water, the difference in the solubility parameter, i.e., heat of

solution per unit volume, is almost constant for any homologous hydrocarbons, and the heat term is proportional to the molal volume, namely, to the hydrocarbon chain length. Actually, the logarithm of the solubility of hydrocarbons or paraffin chain compounds decreases linearly with the increase of hydrocarbon chain length.

This tendency is opposed by the influence of the hydrophilic portion in the case of a surface active agent and shows moderate concentration of single dispersion. The saturation concentration of singly dispersed species (CMC) of the surface active agent, of course, changes very much with the length of hydrocarbon chain, just as the solubility of hydrocarbons or aliphatic alcohols changes very much with the length of hydrocarbon chain.

If no salt is added to the solution, the concentrations of gegenions and surface active ions which are in an equilibrium with excess charged solid ionic surface active agent are practically the same. On the one hand, electrical attraction between gegenions and the excess solid decreases the equilibrium concentration of gegenions in the bulk which are in equilibrium with gegenions in the solid phase, and on the other hand, the electrical repulsion between surface active ions in the bulk and charged solid increases the dissolution tendency of the surface active ions which are also in equilibrium with surface active ions in the charged solid. If salt is added, the concentration of gegenions increases and that of paraffin chain ion decreases. The electrical potential on the excess ionic surface active agent decreases also by the progressive fixing or approach of gegenions to the solid surface. This decrease in electrical potential increases the solvency of gegenions and decreases that of paraffin chain ions. It is clear from the above discussion that the saturation concentration of a singly dispersed ionic agent is roughly the geometrical average of the saturation concentration of the corresponding inorganic salt and a hydrocarbon of the same chain length; and the concentration of singly dispersed paraffin chain ions sensitively decreases with an increase of the concentration of gegenions, but the CMC of a nonionic agent is not affected primarily by the addition of salt.

As described above, surface active agents possess a duality and asymmetry of properties. These opposing tendencies are very asymmetrically distributed and may be separately and simultaneously satisfied (2). Therefore, surface active agents have a very strong tendency for adsorption and orientation at the interface from aqueous solution, and the free energy of the system decreases as a result of adsorption. As the adsorption of hydrocarbon chains arises from the strong cohesive force between the water molecules, there is no positive adsorption at hydrocarbon-air interface except in the case of fluorocarbon compounds which have smaller intermolecular force than hydrocarbons.

It is this same combination of properties which is responsible for the characteristic surface or interfacial tension depression and the powerful emulsifying, wetting, dispersing, and foaming abilities of their solutions (2). However, in the bulk of the solution, where there are no surfaces on which adsorption can occur, the paraffin chain molecules (ions) will form aggregates above a certain concentration; that is, micelle formation occurs at a certain concentration at which the (electro) chemical potential of paraffin chain molecule (ions) in the solute state is equal to the (electro) chemical potential of paraffin chain molecule (ions) in the micellar state. The introduction of an aggregate of paraffin chains into which water does not penetrate is thus accomplished with a much smaller expenditure of free energy than would be required if the chains were introduced as separated single chains. The compromise between the segregation of water and hydrocarbon chains and the solvency of the hydrophilic portion of the surface active agent is brought about by the aggregation of the oleophilic portions which are so grouped that the exterior of the aggregate is composed of the hydrophilic portions of the molecules. The shorter the chain, therefore, the smaller will be the reduction of free energy of the system resulting from aggregation and the higher the concentration necessary to produce micelle formation. The fact that there is no clear evidence for the existence of micelles in solutions of paraffin chain salts with less than 4 carbon atoms in the chain is due either to the fact that sufficiently high concentrations, about 3 moles/liter or 40 volume per cent in solution, are unattainable or that energy of aggregation is not big enough to suppress the thermal random mixing motion of molecules. A very high solute concentration in the bulk also changes the solvent property in the direction of being more oleophilic, i.e., less favorable for micelle formation. In solutions of weak electrolytes, e.g., of butyric acid (6, 7), micelles still form. Butanol is also not infinitely miscible with water. The solubility of butanol in water is about 0.97 mole/liter.

A liquid state model for the micelle is supported by the fact that the micelle-forming ion can mix with various additives, forming mixed micelles (8), and by solubilization phenomena exhibited by micellar solutions. It is not necessary that the substance dissolved in this way itself be a liquid; solute (liquid or solid) in solution is in the liquid state. Azobenzene and crystalline derivatives of this compound are dissolved in solutions of paraffin chain salts (2). When both solutes are precipitated by cooling, they are usually easily separated by solution of the azobenzene derivative in an organic solvent and do not, therefore, form solid solution or compound crystalline phases. It seems conclusive that the solvent properties of the micelle are due to its liquid nature (2). The remarkable difference between the liquid state and the solid state

is that a solute does mix with various solvents of markedly different molecular sizes and exhibits similar partial molal volumes close to the molal volumes of the solute in the pure state (9), but in the solid state the solute can hardly form mixed crystals with molecules of different sizes and shapes.

Hence, it seems probable that the micelle is in a liquid state and that the structure of the interior resembles that of a liquid paraffin. The structure will be more organized, however, than liquid paraffin because of the hydrophilic group anchored on the micelle surface. The structure of a liquid paraffin may itself be rather more highly organized than it has been supposed, for the paraffin chain is not freely rotating but rather vibrating in its *trans* or *gauche* form (10). The *trans* form is about 800 cal/mole more stable than the *gauche* form. Even a small change in bond angle also needs a very large energy. A rather straight zigzag chain structure for hydrocarbons has become more widely accepted nowadays. A completely flexible model is certainly an overestimation of flexibility and configurational number.

It has been assumed generally that solutions of surface active agents behave as singly dispersed systems up to the CMC. Osmotic coefficient measurements clearly support this view (11). The colligative properties of solutions of surface active agents do not deviate by more than about 5% from those of ideal 1:1 electrolytes until the CMC is reached (12). But, as revealed by equivalent conductivity measurements (11, 13), there are some surface active agents which show dimerization. The dimerization process may not be a universal phenomenon in solutions of surface active agents, but may depend largely on the molecular type of the surface active agent. If the hydrocarbon chain is sufficiently long, the free energy of the system may decrease as a result of dimerization. The large area of contact between two hydrocarbon chains and a sufficient concentration of singly dispersed species are necessary to balance the electrical energy of approach of two ionic groups and a translational entropy decrease of about 20 eu. Thus, the dimerization will occur more favorably if the hydrocarbon chain is longer. The fraction of dimer increases with increasing bulk concentration up to the CMC, and then it may stay almost constant above the CMC. Dimerization may not be the initiation of micellar aggregation, but the process may rather resemble the coexistence of monomer and dimer in the vapor phase of acetic acid, where the hydrogen bond is a driving force for dimerization. If the vapor pressure reaches the saturation vapor pressure, then liquid acetic acid, which is in equilibrium with monomer and dimer, will separate. The formation of micelles will be similar to this phase separation (14), except that it does not lead to an infinite aggregation number for the micelle. Many theories on micelle formation have been based on this