UNIVERSITI PUTRA MALAYSIA

MICELLAR REGION OF IONIC SURFACTANT SOLUTION AND ITS MICROENVIRONMENT PROPERTIES

LAILI BT HJ. CHE' ROSE

FSAS 2001 23

MICELLAR REGION OF IONIC SURFACTANT SOLUTION AND ITS MICROENVIRONMENT PROPERTIES

By

LAILI BT HJ. CHE' ROSE

Thesis Submitted in Fulfilment of the Requirement for the Degree
of Master of Science in the Faculty of Science and Environmental
Studies, Universiti Putra Malaysia

May 2001

Dedicated to Allahyarhamah Hajjah Fatimah Bt Md Sab
In memory of my beloved mother
31 May 1998

"Thank You for your everlasting love and support.
Although you are not able to share my success
I know that you will be very happy for me."
May Allah Bless You Always
Al Fatihah

I Love You So Much, Mak!!

Abstract of thesis presented to the Senate of Universiti Putra Malaysia
in fulfilment of the requirement for the degree of Master of Science

MICELLAR REGION OF IONIC SURFACTANTS SOLUTION AND ITS MICROENVIRONMENT PROPERTIES

By

LAILI BT HJ CHE' ROSE

May 2001

Chairman : Assoc. Prof. Dr. Mohd Zaizi Bin Desa

Faculty : Science and Environmental Studies

The conventional method which have been used most extensively to determine aggregation number, n such as classical and quasi-elastic light scattering suffers from the lack in the determination of n as a function of concentration. It has been proposed that a fluorescence method of micelle-solubilized pyrene and using the ratio of the first and third vibronic bands as an index of the effective local polarity, provides an alternative to the study of the microenvironment of micellar interior.

It is well understood that the addition of a third component, affects not only the critical micelle concentration, cmc and aggregation number but also the microenvironment of the micelle. Compounds such as alcohols which are solubilized in the micelles, directly modify the micelle itself. Addition of salts modifies the electric double layer around a micelle and alters the hydrophobic interaction, which is significant for micelle formation. The variations in the hydrophobic interaction indirectly influence the microenvironment inside the micelles.

With that note, this work is directed to the investigation of the micellar region and the microenvironment property namely micropolarity, of micellar interior of two ionic surfactant, above cmc, upon the addition of a medium chain alcohol, pentanol employing the fluorescence probing method. The ionic surfactants are the negatively charged, sodium dodecyl sulphate, SDS and the positively charged, cetyltrimethylammonium bromide, CTAB.

From the phase diagram studies, the micellar region has been successfully constructed and identified in both aqueous and nonaqueous systems at 30 ^{0}C. The results show that the presence of a polar solvent, glycerol disturbs the stability of the micellar region in both of the ionic surfactant systems. The result also show that the negatively charged, SDS is more superior in solubilizing pentanol than the positively charged, CTAB in the aqueous systems.

From the fluorescence studies, the results show a decrease in the ratio of the vibronic bands at higher pentanol content. The micropolarity of the micellar interior with CTAB is, however, found to be higher than the corresponding one with SDS regardless of the concentration of the ionic surfactant solution. In addition, a transition in the micellar shape is also observed and is further supported by the conductivity studies.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra
Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KAWASAN MISEL LARUTAN SURFAKTAN IONIK DAN CIRI-CIRI MIKROSEKITARANNYA

Oleh

LAILI BT HJ CHE'ROSE

Mei 2001

Pengerusi : **Prof. Madya Dr Mohd Zaizi Bin Desa**

Fakulti : **Sains dan Pengajian Alam Sekitar**

Kaedah konvensional yang telah banyak digunakan untuk menentukan nombor aggregasi, n, seperti pengimbauan cahaya klasik dan quasi-elastik gagal bagi menentukan n sebagai satu fungsi kepekatan. Ada dicadangkan bahawa kaedah pendaflor kelarutan pirena dalam misel dan menggunakan nisbah puncak vibronik pertama dan ketiga sebagai indeks keberkesanan kepolaran pusat, dalam memberikan satu alternatif bagi kajian mikrosekitaran dalaman misel.

Adalah diketahui bahawa penambahan satu komponen ketiga akan memberi kesan bukan sahaja kepada kepekatan kritikal misel, kkm dan nombor aggregasi tetapi juga kepada mikrosekitaran misel. Sebatian-sebatian seperti alkohol yang larut dalam misel akan secara langsung mengubah misel tersebut. Penambahan garam-garam akan mengubah dwilapisan elektrik sekeliling misel dan mengubah saling tindak hidrofobik yang sangat penting dalam pembentukan misel. Perubahan dalam saling tindak hidrofobik ini secara tidak langsung akan mempengaruhi mikrosekitaran dalaman misel.

Dengan itu, kerja ini ditumpukan kepada kajian kawasan misel dan mikrosekitaran seperti kepolaran mikro dalaman misel untuk dua surfaktan ionik, selepas kkm, pada penambahan alkohol berantai sederhana, 1- pentanol dengan menggunakan kaedah prob pendaflor. Surfaktan ionik yang bercas negatif adalah seperti natrium dodesil sulfat, SDS dan yang bercas positif, setiltrimetilammonium bromida, CTAB.

Daripada kajian gambarajah fasa, kawasan misel telah berjaya dibentuk dan ditentukan dalam dua sistem berair dan tanpa air pada 30 ^{0}C. Keputusan menunjukkan kehadiran satu pelarut polar, gliserol menganggu kestabilan kawasan misel kedua-dua sistem surfaktan ionik. Keputusan juga menunjukkan bahawa surfaktan bercas negatif, SDS lebih baik dalam melarutkan 1- pentanol berbanding surfaktan bercas positif dalam sistem berair.

Dari kajian pendaflor, keputusan menunjukkan pengurangan nisbah puncak vibronik pada kandungan 1- pentanol yang tinggi. Kepolaran mikro dalaman misel untuk CTAB walau bagaimanapun, didapati lebih tinggi berbanding dengan SDS tanpa mengira kepekatan larutan surfaktan ionik. Tambahan pula, satu transisi terhadap bentuk misel didapati dan disokong lagi dari kajian kekonduksian.

ACKNOWLEDGEMENTS

I would like to express my most sincere gratitude and deep appreciation to the committee Chairman, Assoc. Prof. Dr Mohd Zaizi Desa for his contribution, guidance, ideas and time towards my project. I would also like to thank the committee members, Assoc. Prof. Dr Anuar Kasim and Assoc. Prof. Dr Faujan B.H.Ahmad .

Special gratitude to my family, and especially my beloved husband; Prof Dr. Hamdan B. Haji Suhaimi, my two beautiful children; Muhammad Haiman and Halili Athirah, my father; Haji Che' Rose B. Baba, my mother in-law; Hajjah Chik Norriah Bt Yan, my brothers and sisters , for their patience and morale support. They are my pride and my joy.

I certify that an Examination Committee met on 14th May 2001 for the final examination of Laili Bt Haji Che'Rose on her Master of Science thesis "Micellar Region of Ionic Surfactant Solution And Its Microenvironment Properties" in accordance with the Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the degree. Members of the Examination Committee are as follows:

Dzulkefli Kuang B Abdullah, Ph D,
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Mohd Zaizi B. Desa, Ph.D,
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Faujan B.H. Ahmad, Ph.D,
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Anuar B. Kassim, Ph.D,
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

....

AINI IDERIS, Ph.D,
Professor/ Dean of Graduate School,
Universiti Putra Malaysia

Date: 25 MAY 2001

DECLARATION

I hereby declare that the thesis is based on my original work except for the quotation and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia, UPM or at any other institution.

....

LAILI BT HAJI CHE'ROSE

Date: 25/5/2001

TABLE OF CONTENTS

Page

CHAPTER

LIST OF FIGURES

LIST OF ABBREVIATIONS

SDS	Sodium dodecylsulphate
CTAB	Cetyltrimethylammonium bromide
RST	Regular Solution Theory
L_1	Normal micelle (o/w microemulsion)
L_2	Reverse micelle (w/o microemulsion)
W/O	Water in oil
O/W	Oil in water

CHAPTER 1

INTRODUCTION

1.1 Amphiphilic Compounds

Amphiphilic compounds or more briefly, amphiphiles, are characterized by possessing in the same molecule two distinct groups which differ greatly in their solubility relationships. Such compounds were termed “amphipathic” by Hartley (1936) to denote the presence of a “lyophilic” group having an affinity for the solvent and a second group, sometimes referred to as “lyophobic”, which is antipathetic to the solvent. Whenever water is the solvent, the two groups are often designated as hydrophilic and hydrophobic portions, or more commonly and perhaps more pictorially as the “head” and the “tail” respectively. The terms “lipophile”, “hydrophobe”, and “amphile’s tail” therefore, are all used in the literature to describe the same part of the amphiphilic compound, and these terms may be regarded as being interchangeable. Similarly, “hydrophile” and “amphiphile’s head” both refer to the same part of the amphiphile and are also interchangeable.

Amphiphilic compounds tend to concentrate as a monolayer at a water interface, with the tendency increasing as both the lipophilic and hydrophilic character of the amphiphile becomes more pronounced. At the interface, amphiphilic compounds are arranged so that the lipophile is removed from the water while the hydrophile remains in contact with the aqueous solution. This molecular orientation is consistent with a number of experimental observations, including the sharp reduction in surface or interfacial tension attending the addition of small quantities of amphiphile to an aqueous phase. Due to this pronounced tendency for amphiphiles to accumulate as a monolayer at an interface, and there to reduce the surface tension, they are sometimes called surface-active agents or, more simply, surfactants (Tadros, 1984).

1.2 Surfactants

Surfactants are among the most demanded products in the chemical industry today. They appear in such diverse products such as in detergents, motor oils , pharmaceuticals, cosmetics and drilling muds used in prospecting for petroleum. More recent investigations

(Rosen, 1985) by researchers are focussing on chemical kinetics and biochemistry due to the amazing properties of the polymeric forms (micelles) of these materials.

Surfactant or otherwise known as *surface - active agent* is a substance that, when present at low concentration in a system, has the ability of adsorbing onto the surfaces or the interfaces of the system and thus altering the properties of those surfaces (or interfaces). The term interface denotes a boundary between any two insoluble phases; the term surface indicates an interface where one phase is a gas, usually air.

Surfactants (Fig. 1.1) have a molecular structure consisting of a group that has low attraction for the solvent, known as the lyophobic (hydrophobic) group, along with a group that has strong attraction for the solvent, called the lyophilic (hydrophilic) group. This characteristic structure is known as amphiphatic structure. The hydrophobic group which is the non-polar portion of the surfactant molecules is usually a long - chain hydrocarbon. The hydrophilic group is an ionic or highly polar portion and depending on the nature of the hydrophilic group, surfactant are categorized (Rosen, 1985) as: