STUDIES ON THE BEHAVIOUR OF ANIONIC SURFACTANT IN ABSENCE AND PRESENCE OF MONOVALENT SALTS IN METHANOL-WATER MIXED SOLVENT MEDIA

A THESIS SUBMITTED TO THE

CENTRAL DEPARTMENT OF CHEMISTRY

INSTITUTE OF SCIENCE AND TECHNOLOGY

TRIBHUVAN UNIVERSITY

NEPAL

FOR THE AWARD OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

BY

TULASI PRASAD NIRAULA

FEBRUARY 2017

DECLARATION

Thesis entitled "**Studies on the behavior of anionic surfactant in absence and presence of monovalent salts in methanol-water mixed solvent media**"which is being submitted to the Central Department of Chemistry, Institute of Science and Technology(IOST), Tribhuvan University, Nepal for the award of the degree of Doctor of Philosophy (Ph.D.), is a research work carried out by me under the supervision of Prof. Dr. Sujeet Kumar Chatterjeeand Dr. Ajaya Bhattarai, Department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Tribhuvan University, Biratnagar, Nepal.

This research is original and has not been submitted earlier in part or full in this or any other form of any university or institute, here or elsewhere, for the award of any degree.

February 2017

……

Tulasi Prasad Niraula
Department of Chemistry
Mahendra Morang Adarsh Multiple Campus,
Tribhuvan University
Biratnagar, Nepal.

RECOMMENDATION

This is to recommend that**Mr.Tulasi Prasad Niraula**has carried out research entitled "**Studies on the behavior of anionic surfactant in absence and presence of monovalent salts in methanol-water mixed solvent media***"* for the award of Doctor of Philosophy (Ph.D.) in **Chemistry** under our supervision. To our knowledge, this work has not been submitted for any other degree. He has fulfilled all the requirements laid down by the Institute of Science and Technology (IOST), Tribhuvan University, Kirtipur, Kathmandu for the submission of the thesis for the award of Ph.D. degree.

Dr. Sujeet Kumar Chatterjee
(Supervisor)
Professor
Department of Chemistry
Mahendra Morang Adarsh Multiple Campus,
Tribhuvan University
Biratnagar,Nepal.

Ajaya Bhattarai

Dr. Ajaya Bhattarai
(Co-Supervisor)
Assistant Professor
Department of Chemistry
Mahendra Morang AdarshMultiple Campus,
Tribhuvan University
Biratnagar, Nepal.

February 2017
February 2017

LETTER OF APPROVAL

On the recommendation of **Prof. Dr. Sujeet Kumar Chatterjee** and **Dr. Ajaya Bhattarai**, this Ph. D. thesis submitted by **Mr.Tulasi Prasad Niraula**, entitled "**Studies on the behavior of anionic surfactant in absence and presence of monovalent salts in methanol-water mixed solvent media**" is forwarded by Central Department Research Committee (CDRC) to the Dean, IOST, Tribhuvan University,for the further processing.

…….

Dr. Megh Raj Pokhrel

(Professor and Head)

Central Department of Chemistry

Tribhuvan University

Kirtipur, Kathmandu

Nepal.

[Date: 30/04 /2017]

ACKNOWLEDGEMENTS

The Present work embodies the results of the research carried out by me at the Department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Tribhuvan University, Nepal, during 2011-2017.

I express my deepest gratitude to **Professor Dr. Sujeet Kumar Chatterjee** (Supervisor) and **Dr. Ajaya Bhattarai** (Co-Supervisor) for guiding me passionately in my work on surface chemistry. I would like to thank them for encouragement, effective guidance and stimulating discussions on different fields of research in these years.

I sincerely thank Chairman, Professors and Staffs of Central Department of Chemistry, Kirtipur, Kathmandu as well as Department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Biratnagar who co-operate me for the research by providing technical support as well as dynamic and positive atmosphere.

I warmly thank my father Kula Prasad Niraula, my mother BalKumari Niraula and my spouse Mana Maya Rijal (Niraula) for patience, understanding, and active support shown by them for my research study.

Lastly I would like to give my special thanks to the senior researcher of our laboratory Dr. Sujit Kumar Shah, Campus Chief and Assistant Campus Chief of Mahendra Morang Adarsh Multiple Campus (Tribhuvan University), Biratnagar, Nepal for their active support and inspiration for the research study.

February 2017

…….

Tulasi Prasad Niraula
Department of Chemistry
Mahendra Morang Adarsh
Multiple Campus
Tribhuvan University
Biratnagar, Nepal.

ABSTRACT

Surfactants are surface active compounds and play important role in different fields like detergency, corrosion inhibition, fertilizers, etc. They form aggregates at a suitable concentration known as micelles and concentration is called critical micelle concentration (cmc). The solvent composition, the temperature and the additives mainly determine physicochemical properties of micelles. Most of the short chain alcohols have the effect of co-solvent and works as water structure breaker. Methanolis the lowest member of alcohol and has the highest relative permittivity. It is completely soluble in water.

The main target of the work was to find the solution properties of sodiumdodecyl sulfate (SDS) in different conditions. The study includes the measurement of the density, the conductivity, the surface tension and the viscosity of SDS solution in pure water and different volume fractions of methanol at different temperature in presence and absence of additives. It also included determination of cmcs and the calculation of different thermodynamic properties.

The density of the solution of pure SDS as well as in the presence of CTAB decreased with increase in temperature and increased in the amount of methanol in water. The partial molar volume was directly proportional to the temperature. With the increase in the concentration of surfactant in a solvent at the fixed temperature, the density increased.

The specific conductivity of SDS in pure water and four volume fractions of methanol in the presence and absence of salts at four different temperatures were measured and the cmcs were calculated. The conductance increased with increase in the concentration of surfactant, increase in temperature and addition of salts. The cmc increased with increase in temperature and volume fraction of methanol but decreased in the presence of additives. The order of cmc in the presence of studied salts was NaCl>NaBr> KCl >KBr. With the help of cmc, different thermodynamic parameterswere determined. Compensation temperature (T_C), and solute-solute interaction (σ) are also calculated.

Different solvent parameters namely Relative permittivity, Reichardt's parameter, Hildebrand parameter and Gordon parameter were correlated withGibbs free of micellisation($\Delta G_{\mathrm{m}}^{\circ}$).The correlation of$\Delta G_{\mathrm{m}}^{\circ}$with solvophobic parameterS_{p} is calculated. The S_{p}values of the hydrocarbon in methanol-water mixture affect the ionization degree of SDS in the presence and the absence of salts.

The surface tension of solution of SDS was measured and cmc as well as some surface properties were also calculated, in pure water, and different volume fractions of methanol at four different temperature.

The viscosities of surfactant solutions were measured and values of the cmcsas well as the viscosity coefficient B values were calculated.

Key words: SDS, Methanol, cmc

LIST OF ABBREVIATIONS

ABS	Alkyl benzene sulphonate
AMT	Amitriptyline hydrochloride
CMC	Critical micelle concentration
CPC	Cetylpyrimidium chloride
DLS	Dynamic light scattering
DTAB	Dodecyltrimethyl ammonium bromide
CTAB	Cetyltrimethylammonium bromide
EM	Erythromycine
FCC	Face centre cubic
IFT	Interfacial tension
ITC	Internal titration calorimetry
LABS	Linearalkylbenzenesulphonates
NMR	Nuclear magnetic resonance
OT	Aerosol
PDN	Pendant drop number
SANS	Small angle neutron scattering
SDS	Sodium dodecyl sulphate
SLS	Sodiumlaurylsulphate
SDT	Sexually transmitted diseases
TTA	Tetradecyltrimethylammoniumbromide
VFT	Viscous flow time

LIST OF SYMBOLS

α	Micelle ionization fraction
$\Delta G_{\mathrm{m}}^{\circ}$	Standard free energy of micellization
$\Delta H_{\mathrm{m}}^{\circ}$	Standard enthalpy of micellization
$\Delta S_{\mathrm{m}}^{\circ}$	Standard entropy of micellization
Γ_{max}	Maximum surface excess concentration
γ	Surface tension
R	Universal gas constant
T	Absolute temperature
π_{cmc}	Surface pressure
C	Surfactant concentration
A_{min}	Area occupied per surfactant molecule
P	Packing parameters
γ_0	Surface tension of water
γ_{cmc}	Surface tension of surfactant solution at the cmc
$\Delta G_{\mathrm{ads}}^{\circ}$	Standard free energy of adsorption
$\Delta G_{\mathrm{trans}}^{\circ}$	Standard free energy of transfer
β	Counter-ion binding parameter
κ	Conductivity (Specific conductivity)
λ_{m}	Molar conductivity
V_{B}	Apparent molar volume
T_{c}	Compensation temperature
σ	Solute-solute interaction parameter
$\Delta_{\mathrm{m}} C_{\mathrm{p}}^{\circ}$	Heat capacity of micellisation
S_{p}	Solvophobic parameter
$E_T(30)$	Reichardt's parameter
δ	Hildebrand parameter
G	Gordon Parameter
D	Relative Permittivity

LIST OF TABLES

LIST OF FIGURES

TABLE OF CONTENTS