

**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
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**FOR THE AWARD OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY**

**BY
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DECLARATION

This 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 Chatterjee and 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.

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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.

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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.

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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. Methanol is 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 sodium dodecyl 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 $\text{NaCl} > \text{NaBr} > \text{KCl} > \text{KBr}$. With the help of cmc, different thermodynamic parameters were 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 with Gibbs free of micellisation (ΔG_m°). The correlation of ΔG_m° with solvophobic parameter S_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 cmc as 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
ΔG_m°	Standard free energy of micellization
ΔH_m°	Standard enthalpy of micellization
ΔS_m°	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
$\Delta G_{\text{ads}}^\circ$	Standard free energy of adsorption
$\Delta G_{\text{trans}}^\circ$	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
$\Delta_m C_p^\circ$	Heat capacity of micellisation
S_p	Solvophobic parameter
$E_T(30)$	Reichardt's parameter
δ	Hildebrand parameter
G	Gordon Parameter
D	Relative Permittivity

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