

**A MINOR RESEARCH PROJECT ON
“SELF ASSEMBLY OF SURFACTANT IN MIXED
SOLVENTS.**

SUBMITTED BY

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DECLARATION

I hereby declare that the Minor research Project entitled “ “Self assembly of surfactant in mixed solvents”, completed and written by me and has not previously formed the basis for the award any Degree or Diploma or other similar title of this or any other university or examining body.

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FINAL REPORT FOR MINOR RESERCH PROJECT

Final report for the academic year : March 2008 to April 2010

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DETAILS:

We have studied the micellization of surfactants SDS, CTAB and tweens-80 using a series of Ethylene glycol/water and formamide/water mixed solvents using surface tension, viscosity and conductance measurements. The results are compared with those reported in pure water for the same surfactants. The critical micelle concentration (cmc) shifts to lower values upon increasing the ratio of Ethylene glycol in the Ethylene glycol /water mixed solvent, while the cmc changes in an opposite way with increasing formamide. Contrary to Ethylene glycol , the formamide/water mixed solvent seems to become a better solvent for the surfactant compared to water and thus disfavors the formation of micelles. We have tried to provide a comprehensive picture of how the presence of cosolvents affects the micelle formation.

KEYWORDS: Surfactant, cosolvents, micellization, critical micelle concentration

INTRODUCTION:

Surfactant forms micelles in aqueous solutions due to the reduction in the free energy when transferring the hydrophobic part (or hydrocarbon chain) from the polar solvent to the micellar interior, the so-called “hydrophobic effect”. The different association behaviours of surfactants in water and other solvents have stimulated the interest to elucidate how the solvent properties influence aggregation, and many studies have been performed to gain information on the role of the solvent in the aggregation phenomenon of amphiphiles. A number of papers on micellization of ionic and nonionic surfactant in mixed solvents have been published [1- 5].

The addition of polar organic solvents, such as ethylene glycol or formamide, would provide extra degrees of freedom in tailoring the solution properties. For example, pharmaceutical formulation for drug delivery uses cosolvents such as glycerol and ethanol in order to improve the solubility of the active compounds and/or to aid the sensory perception. There is enough experimental evidence supported by theory on the surfactant self-aggregation in solvents such as ethylene glycol and formamide, so that both micelles and lyotropic liquid crystals are formed. Evans et al. [6] established that the specific properties of water are not indispensable to promote surfactant self-assembly. Investigations of micellization in nonaqueous polar solvents, such as ethylene glycol, glycerol and formamide, which have properties resembling

those of water, have shown that a solvent requires three conditions to induce surfactant aggregation (i) a high cohesive energy, (ii) a high dielectric constant, and (iii) a high hydrogen-bonding ability.

This energy gain correlates with the solvent property. A measure of the solvent property is proposed as cohesive energy density, $\zeta/V^{1/3}$, where ζ is the surface tension and V is the molar volume of the solvent. For example, the values for water and ethylene glycol are 27 and 12 $\text{dyn}\cdot\text{cm}^{-2}\cdot\text{mol}^{1/3}$, respectively. Experimental results show that the critical micelle concentration (cmc) increases with decreasing this parameter, suggesting that the free energy gain of micellization, which decreases proportionally to the logarithm of the mole fraction of surfactant at cmc,⁵ decreases with decreasing the parameter, $\zeta/V^{1/3}$. It was reported that the $\zeta/V^{1/3}$ value should be higher than 10-11 $\text{dyn}\cdot\text{cm}^{-2}\cdot\text{mol}^{1/3}$ for micellization.

It was also reported that the formation of liquid crystals is interrupted upon addition of a polar nonaqueous solvent. However it has not been studied show the liquid crystals are decomposed by the polar nonaqueous solvent. It is well-known that the cloud temperature of aqueous solution of a polyoxyethylene -type surfactant lowers or raises depending on the types of the added inorganic salts, which is called as the salting-out or -in effect, respectively.

The salt effects are related to the adsorption/depletion of the salt at the surfactant film.¹² The similar effects are also observed when alcohols are used instead of a salt. Polyols such as glycerol, poly(ethylene glycol), D-sorbitol etc. show a "salting-out" effect whereas *n*-alcohols or glycols show the opposite effect. In a water/CmEOn-type surfactant/hydrocarbon system, a structure of microemulsions varies from oil-in-water (O/W) to water-in-oil (W/O) type with increasing temperature at low surfactant concentration. When a mixture of water and glycerol,¹⁶ or propylene glycol and glycerol, for instance, is employed instead of pure water, the same structural transition of microemulsions from O/W to W/O is observed with changing the composition of the mixed solvent at constant temperature. The addition of salt also causes the same structural transition of the microemulsions if the salt has the salting-out effect. However it is still unclear

that the effect of added alcohol on the surfactant hydrophilicity is the same as that of inorganic salts.

In the template synthesis of inorganic materials, morphology and dynamic properties of surfactant micelles play an important role. They determine not only the pore size distribution but also the pore ordering. In recent years, the surfactant aggregation solutions have attracted considerable interests. In the template synthesis of nano porous materials, alcohols are often used as additives. Numerous studies have been carried out to elucidate the effect of the hydrophobic interaction of surfactants on the micelle formation in mixed aqueous/organic solutions.

To clear up the details of the interactions involved in the so-called solvophobic effect, many investigations have been carried out where water is partially replaced with another polar solvent. This reasonable approach permits an exploration of a range of compositions where the solvent characteristics change in a gradual manner. The micellar aggregation of surfactants in polar solvents other than water has been mainly studied by using ionic surfactants []. These studies suggest that the driving force for the solvophobic effect has essentially the same origin as the hydrophobic effect, i.e. the large cohesive energy of the solvent. Micellization of nonionic surfactants in polar solvents has been much less studied, and often the results that appear in the literature are contradictory. Studied the micelle formation of monododecyl octaethylene glycol (C12E8) and monododecyl hexaethylene glycol (C12E6) in water mixed with ethylene glycol, sorbitol or glycerol, using small angle neutron scattering. They found that the size of the micelles increased with the addition of cosolvent. This behaviour was attributed to a decreasing hydration of the polyoxyethylene groups due to the interaction between water and the cosolvent, causing a reduced curvature in the micellar aggregate. On the other hand, it was observed that the micellar size of C12E8 decreased with the addition of glycerol in the mixed solvent. They ascribed this fact to a reduction of the micelle solvation in the solvent system. Recently some reported a study on the effect of several cosolvents, including formamide, ethanol, and glycerol, on the micellar structure of Pluronic P105. This investigation showed that the micelle association numbers become smaller in the presence of formamide or ethanol. This behaviour was interpreted on the basis of a reduction of the interfacial tension between the hydrophobic chains and the

solvent. As a consequence, the formation of smaller micelles becomes more favourable energetical.

In this context, we have studied systematically aggregation behavior of both ionic and nonionic surfactant by changing solvent composition in mixed solvents consisting of water and one of the following cosolvents: ethylene glycol or formamide[7-19] (with dielectric constants below and above water, respectively). The principal means of characterization are surface tension, conductance and viscosity measurements.

EXPERIMENTAL

Materials

The cationic surfactant hexadecyltrimethylammonium bromide ($C_{16}TABr$), anionic sodium dodecyl sulfate (SDS) and polyoxyethylene sorbitan monooleate (Tween-80) were highly pure samples from Sigma/Aldrich. Their purities were ascertained by surface tension measurements; no surface tension- log concentration plot for any surfactant used in this study showed a minimum. Triple distilled water from an all Pyrex glass apparatus was used for the preparation of solutions.

Methods

Surface tension

The surface tension of aqueous solutions of single surfactants at various concentrations was determined by using the drop number method. All measurements were carried out at 30°C. The CMC values were determined at sharp break points in surface tension against log concentration curves for individual surfactants.

Conductance

Conductometric measurements were made with a digital Microprocessor Based Conductivity / TDS Meter Model 1601 conductivity meter (Esico, India) using a dip-type cell at 30°C. All measurements were done in a jacketed vessel, which was maintained at the appropriate temperature ($\pm 0.1^\circ\text{C}$). The errors in the conductance measurements were within $\pm 0.5\%$. The conductance was measured after thorough mixing and temperature equilibrium at each dilution.

Viscosity

The viscosity measurements were made using an Ubbelohde suspended level capillary viscometer. The viscometer was always suspended vertically in a thermostat with a temperature stability of $\pm 0.1^\circ\text{C}$ in the investigated region. The viscometer was cleaned and dried every time before and after each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stopwatch.

RESULTS AND DISCUSSION

Surface tension

The surface tension (γ) of surfactant solutions was measured for a range of concentrations above and below the critical micelle concentration (CMC). A linear decrease in surface tension was observed with increase in surfactant concentrations for all the surfactants up to the CMC, beyond which no considerable change was noticed. This is a common behaviour shown by surfactants in solution and is used to determine their purity and CMCs. The CMC data obtained from the break point in the γ - log concentration plots are recorded in Table I. CMC values for all the surfactants are in reasonable agreement with the literature values.

A representative plots for Tween-80 in water and ethylene glycol/water mixed solvent is shown in Figure 1. As depicted from the figure the CMC values shifts towards lower Tween-80 concentration with increasing the ethylene glycol concentration in the mixed solvent. While increasing the formamide content in the mixed solvent shifts the CMC towards higher surfactant concentration (Figure 2). The formamide/water mixed solvent seems to become a better solvent for the surfactants compared to water and thus disfavours the formation of micelles. Addition of formamide to water reduces the solvophobicity and increases the solubility of surfactant. This in turn lowers the interfacial tension between the hydrophobic chains and the solvent, so that shrinking and disruption of micelles becomes more energetically favourable than in plain water.

In case of ionic surfactants the main effect of the cosolvent is considered to be the change of the dielectric constant of the medium, which in turn affects the electrostatic interaction in

solution. The ethylene glycol dielectric constant ($\epsilon_r = 42.5$) is substantially lower than that of water ($\epsilon_r = 78.5$); consequently, increasing the glycerol concentration enhances the electrostatic interactions in solution, which opposes the self-aggregation of surfactant molecules.

Conductance

Conductivity measurements were performed for ionic surfactants at 30°C in order to evaluate the CMC and the degree of counter ion dissociation, β . It is known that the specific conductivity is linearly correlated to the surfactant concentration in both the premicellar and in the post micellar regions, being the slope in the premicellar region greater than that in the post micellar region. The intersection point between the two straight lines gives the CMC while the ratio between the slopes of the post micellar region to that in the premicellar region gives counter ion dissociation, β . The values of CMC and β at various temperatures for the ionic surfactants are recorded in Table I. This results support the findings from surface tension measurements.

Viscosity

We have used viscosity measurements to obtain the concentration at which the sphere-to-rod transitions of the micelles of various surfactants occur. Relative viscosities of surfactant solutions at different concentrations of C₁₆TABr, SDS and Tween-80 were carefully examined at 30°C and the representative plots of results for C₁₆TABr and Tween-80 obtained in presence of ethylene glycol/water and formamide/water mixed solvents are shown in Figure 3 and 4 respectively. All the measurements were made above the critical micelle concentration (CMC) for each surfactant. The results obtained were quite interesting. As seen from the Figure 3 and 4 the relative viscosity increases gradually with increase in surfactant concentration. Addition of glycerol content in the mixed solvents results in an increase in micellar size for nonionic Tween-80 as indicated by an increase in viscosity, while in case of ionic surfactant

C₁₆TABr the effect is almost negligible. Opposite to ethylene glycol, addition of formamide in the mixed solvent, favors the disruption of micelles as indicated by the significant decrease in viscosity. A close inspection of Figure 3 reveals that the viscosity of Tween-80 increases by two orders of magnitude in the presence of however after a certain increase in ethylene glycol content results in formation of lamellar liquid crystals, which support the claim that there is a reduction of specific surface area and surface curvature as ethylene glycol is added. However the presence of ethylene glycol shows opposite trend in case of ionic surfactant compared to the non-ionic one. In the case of ionic surfactant in addition to the change in dielectric constant of the medium, the increased repulsion among the ionic head groups also causes an increase of the micellar curvature, leading to the formation of smaller aggregates. Hence, the extent of glycerol effects and the mechanism through which they are supposed to act, depend on the considered surfactant.

The experimental evidence shows that increasing formamide content in mixed solvent with water has similar effect on both ionic and non-ionic surfactant; causing the disruption of micelles.

CONCLUSIONS

The effects of polar solvents such as ethylene glycol and formamide on the micellization of ionic and nonionic surfactants in water have been investigated as a function of the cosolvent content in the mixed solvent using surface tension, conductance and viscosity measurements. The addition of formamide to water causes micellar disruption, which is attributed to lower hydrocarbon-solvent interfacial tension and a reduction in the solvophobic effect, while the progressive increase of ethylene glycol in water- ethylene glycol mixed solvent reduces the hydration of surfactant head groups and induces smaller surfactant surface areas, which in turn causes micellar growth. These basic findings can be used to tune the surfactant properties for end application.

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Table – 1 Critical Micellar Concentration of surfactant with different cosolvents at 303.15K.

Surfactant	Mixed solvent	CMC From Sp. Conductance	Sp. Cond β	Surface tension β
SDS	95% Water + 5 % EG	8mM	0.6783	0.3750
	90% Water + 10% EG	7mM	0.6857	0.5000
	85 % Water + 15% EG	5mM	0.7125	0.6250
	95% Water + 5 % Formamide	9mM	0.4040	0.4432
	90% Water + 10% Formamide	11mM	0.4608	0.5000
	85 % Water + 15% Formamide	13mM	0.5000	0.5357
CTAB	95% Water + 5 % EG	1.7mM	0.4807	0.4300
	90% Water + 10% EG	1.4mM	0.6250	0.6300
	85 % Water + 15% EG	1.2mM	0.6986	0.7053
	95% Water + 5 % Formamide	1.4mM	0.5625	0.6561
	90% Water + 10% Formamide	1.6mM	0.6376	0.6819

	85 % Water + 15% Formamide	1.8mM	0.7142	0.7058
Tweens	95% Water + 5 % EG	0.012mM		0.4545
	90% Water + 10% EG	0.01mM		0.5000
	85 % Water + 15% EG	0.008mM		0.6000
	95% Water + 5 % Formamide	0.01mM		0.2962
	90% Water + 10% Formamide	0.013mM		0.3600
	85 % Water + 15% Formamide	0.017mM		0.5100

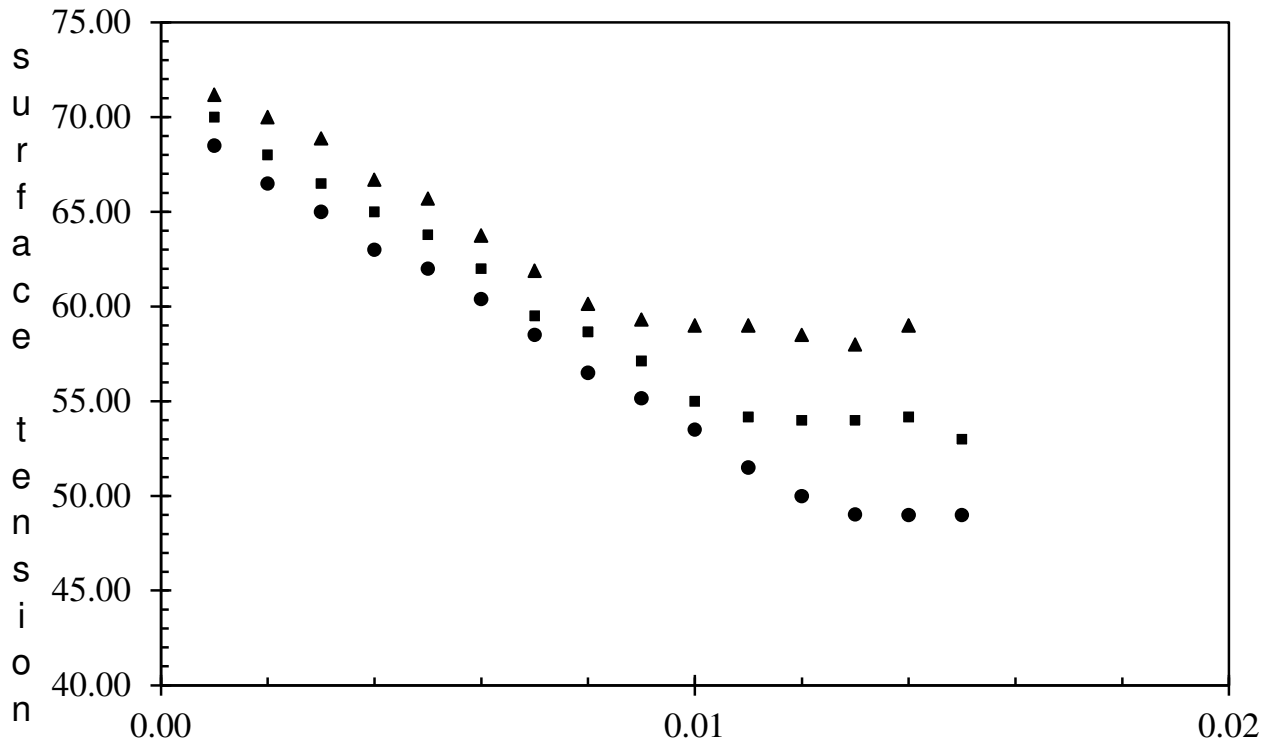


Figure – 1 :Surface tension of Tweens -80 and EG in water at 303.15K. .i.(●)5

%EG+ 95%Water, ii. (■) 10%EG + 90%Water and iii. (▲) 15% EG +

85%water

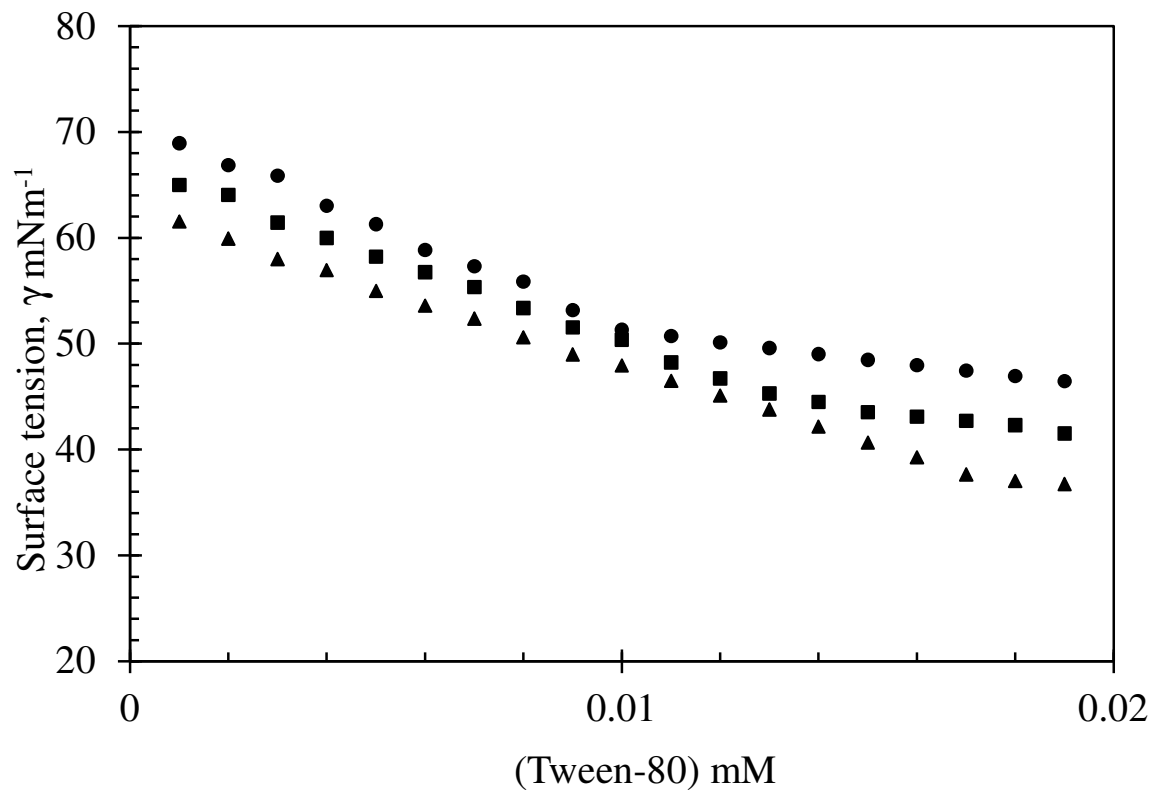


Figure – 2 : Surface tension of tweess -80 for Formamide in water. i. (●)5

%Formamide+ 95%Water, ii. (■) 10%Formamaide + 90%Water

and iii.(▲) 15% Formamide + 85%water at 303.15K.

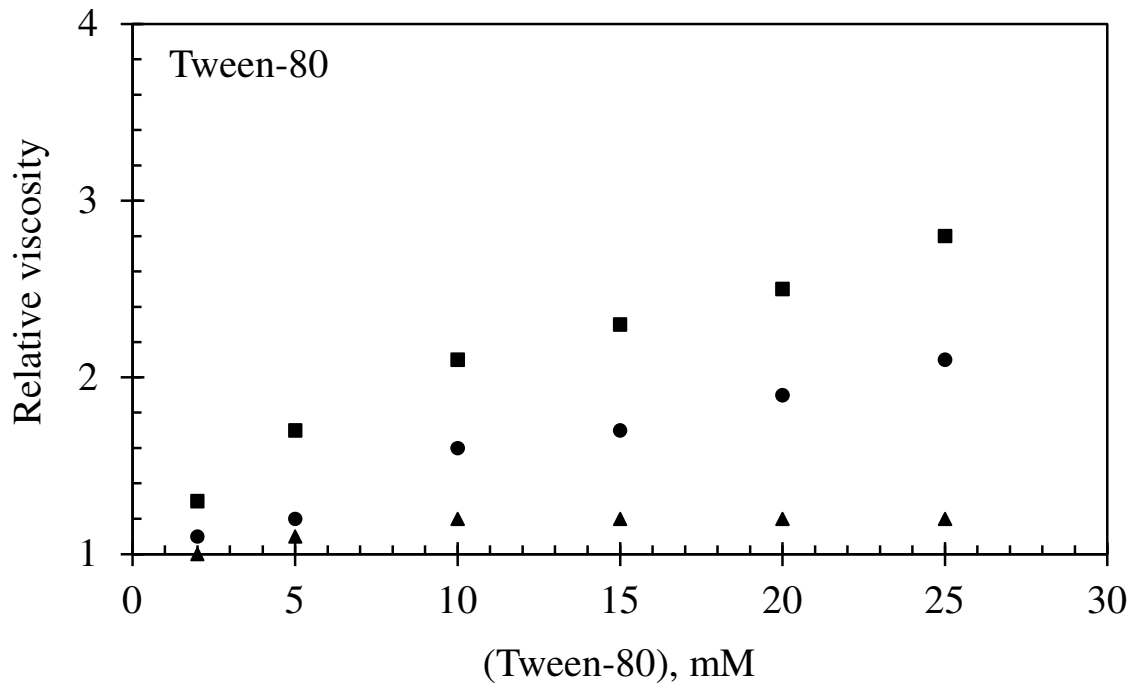


Figure- 3 : Relative viscosity of tweens -80 in water, EG and Formamide at

303.15K. i. (●)Water, ii. (■) 15%EG + 85%Water and iii. (▲) 15%

Formamide + 85%water at 303.15K.

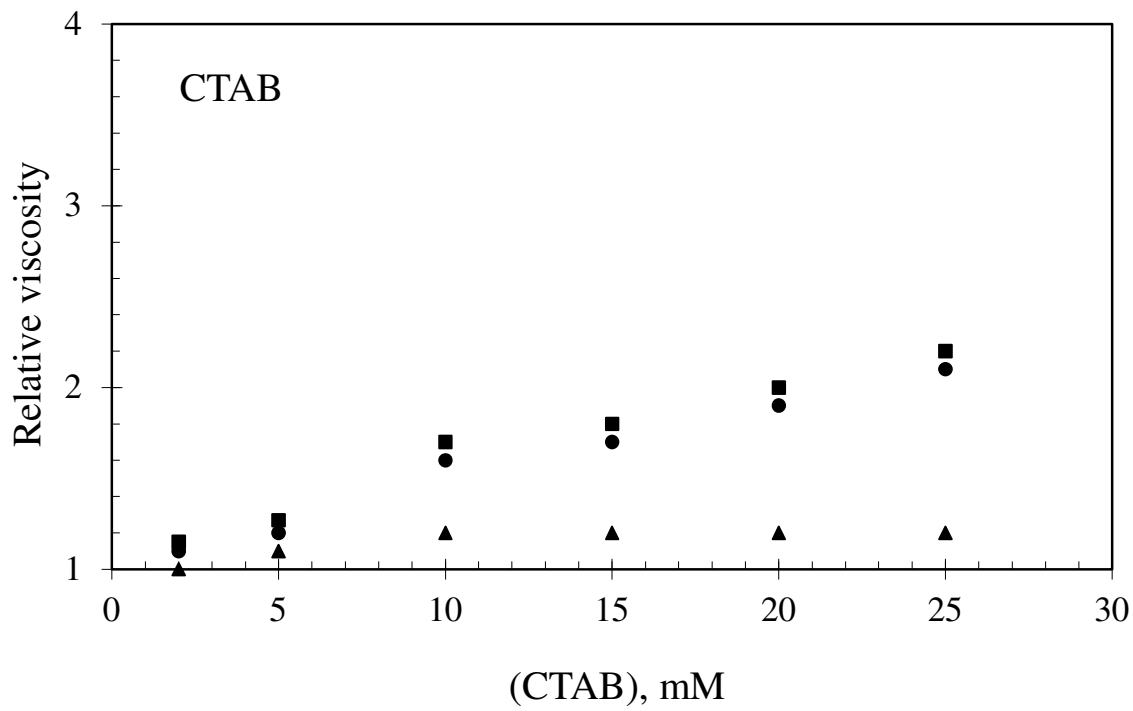


Figure – 4 : Relative viscosity of CTAB in i.(●) water, ii.(■) 15%EG + 85 % water and
iii. (▲) 15% + 85% water at 303.15K.

PUBLICATION

INTRODUCTION

EXPERIMENTAL AND MATERIAL

RESULT AND DISCUSSION