

Wetting of PTFE Surface by Mixed Surfactant Solutions in the Presence of Electrolyte

A Thesis submitted to the

National Institute of Technology, Rourkela

In partial fulfilment of the requirements

of

Bachelor of Technology (Chemical Engineering)

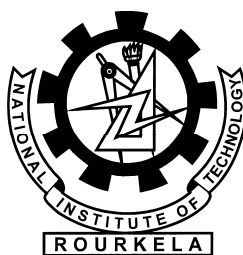
By

Saswati Sunayana

Roll No. 10600020

Under the guidance of

Dr. Santanu Paria



DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

ORISSA -769 008, INDIA

2010



**DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY,
ROURKELA - 769 008, INDIA**

CERTIFICATE

This is to certify that the thesis entitled “Wetting of PTFE surface by mixed surfactant solutions in the presence of electrolyte”, submitted by Saswati Sunayana for the requirements of bachelor’s degree in Chemical Engineering Department of National Institute of Technology, Rourkela is an original work to the best of my knowledge, done under my supervision and guidance.

Date-11/05/10

**Dr. Santanu Paria
Department of Chemical Engineering
National Institute of Technology,
Rourkela - 769008**

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Saswati Sunayana

CONTENTS

TOPIC	PAGE NUMBER
ABSTRACT	i
LIST OF FIGURES	ii
LIST OF TABLES	v
LIST OF SYMBOLS	vi
CHAPTER 1: INTRODUCTION	1 – 3
1.Importance of wetting	1
1.1.Wetting of a solid surface	1
1.2. Effect of surfactants on wettability	2
1.3. Surfactant adsorption	2
1.3.1. Types of surfactants	2
1.3.2. Mixed surfactant system	3
1.3.3. Application of mixed surfactant system	3
CHAPTER 2: LITERATURE REVIEW	4 – 12
2.1. Single surfactant system	4
2.2. Mixture of surfactants	7
2.3. Effect of additives	10
2.3.1. Effect of alcohols	10
2.3.2. Effect of electrolytes	11
CHAPTER 3: EXPERIMENTAL WORK	13 – 14
3.1. Materials	13
3.2. Methods	14
CHAPTER 4: RESULT AND DISCUSSION	15 – 29
4.1. Solution behaviour of pure surfactants	15
4.2. Wetting behaviour of pure surfactants	16
4.3. Solution behaviour of the mixed surfactant system	18
4.4. Wettability of mixed surfactant system	20

4.4.1. Adsorption at solid-liquid and liquid-air interface	21
4.4.2. Critical surface tension	22
4.4.3. Linearity of relation between surface tension and interfacial tension	23
4.4.4. Work of adhesion on Teflon surface	24
4.5. Electrolyte effect on mixed surfactant system	25
4.5.1. Solution behavior mixed surfactant system with electrolyte	26
4.5.2. Wettability of mixed surfactant system with electrolyte	29
CHAPTER 5: CONCLUSION	30 - 31
REFERENCE	32 – 35

ABSTRACT

Improving the wettability of hydrophobic surfaces has wide ranges of applications, and mixed surfactant systems are promising to improve the interfacial phenomena including wetting. In this study mixture of cationic (Cetyltrimethyl ammonium bromide, CTAB) and non-ionic (Igepal-630) surfactants have been studied and compared with the pure surfactants. The nonideal behaviour of the mixture indicates the presence of synergism. Another point of attraction for the investigators has been the effect of additives in surfactant solution. Presence of electrolyte enhances the wetting property very effectively, as proved from previous studies. This report mainly focuses on the change in CMC values as well as wetting property of a mixed surfactant system. It is observe the use of electrolyte, further reduce the CMC than the mixed surfactant systems. The main objective of this study is to provide insight on the wetting of hydrophobic surface in the presence of mixed surfactant system + electrolyte.

List of figures

Figure no.	Title	Page no.
2.1.	Contact angles (θ) of solid/n-C ₁₂ /brine systems as a function of: (i) ionic strength; (ii) C _{SDS} ; and (iii) C _{NaCl} + C _{SDS} . (Serrano-Saldaña et al., 2004)	4
2.2.	Contact angle relationship with time of C ₁₂ E ₅ on Teflon AF surface (Dutschk et al., 2003)	5
2.3.	Contact angle relationship with concentration of SDS (Dutschk et al., 2003)	5
2.4.	Surface tension, γ_L , of surfactant solutions vs. the logarithm of surfactant concentration, log m _S . (●) SDS, (■) SDOSS, (▲) TX100 (Simončič and Rozman, 2007)	6
2.5.	The relationship between the values of the surface tension (γ_{LV}) of aqueous C ₁₂ (EDMAB) (□) and BDDAB (○) solutions and the values of the contact angle (θ) of aqueous C ₁₂ (EDMAB) (■) and BDDAB (●) solutions for the PTFE surface and the concentration of the surfactants (log C). (Harkot and Janczuk, 2009)	6
2.6.	Gibbs' adsorption isotherms for Span 20 (▲) and Tween 20 (●) (Kim and Hsieh, 2001)	7
2.7.	The relationship between the contact angle, θ , and logC (where C is the total concentration of the mixture) for different values of the monomer mole fraction of CTAB, α , in CPyB and CTAB mixture (for PTFE). (Szymczyk et al., 2006)	8
2.8.	The relationship between the contact angle, θ , and monomer mole fraction of CTAB, α , in TX100 and CTAB mixture (for PTFE) at constant total mixture concentration, C, equal to 10 ⁻⁶ (curve 1), 10 ⁻⁵ (curve 2), 5×10 ⁻⁵ (curve 3) 10 ⁻⁴ (curve 4) and 2×10 ⁻⁴ M (curve 5). (Szymczyk and Janczuk, 2006)	8
2.9.		9

2.10.	The relationship between $\cos\theta$ (θ —contact angle) and logarithm C for different values of the mole fraction (α) of SHDSs in SDDS+SHDSs mixture (Zdziennicka et al., 2003)	10
2.11.	Dependence between the measured values of the contact angle (θ) and the propanol concentration. Curves 1, 2, 3 and 4 correspond to the constant values of CTAB equal to 1×10^{-5} , 1×10^{-4} , 6×10^{-4} and 1×10^{-3} M, respectively. (Zdziennicka and Janczuk, 2008)	11
2.12.	Dependence of cmc of DTAB solutions on alcohol content. (Tomi et al.)	12
3.1.	Plot of advancing contact angle (θ_A) for different electrolytes (NaCl, CaCl ₂ , and Na ₂ SO ₄) in the presence of SDBS and CTAB solution on the Teflon surface. (Chaudhuri and Paria, 2009)	13
3.2.	Photograph of Surface tensiometer	14
4.1.	Photograph of video based optical contact angle meter	15
4.2.	Change of surface tension with log C for CTAB and Igepal-630	17
4.3.	Change in contact angle with change in log C for CTAB and Igepal-630	18
4.4.	Variation of adhesional tension with surface tension for CTAB and IGEPAL	19
4.5.	Variation of CMC of mixed surfactant system with varying micellar mole fraction	20
4.6.	Change of contact angle θ with respect to changing concentration C of surfactant.	21
4.7.	Variation of adhesional tension with varying surface tension	22
4.8.	Relationship between inverse of surface tension with $\cos\theta$	23
4.9.	Change in interfacial tension with change in log C thus determining critical surface tension	24
4.10.	Linear relation between surface tension and interfacial tension	25
4.11.	Change of work of adhesion with concentration	26
4.12.	Change of surface tension with concentration of surfactant for a	

	particular value of concentration of electrolyte	
4.13.	Change of contact angle with concentration of surfactant for a particular value of concentration of electrolyte	27
4.14.	Change of adhesional tension with surface tension for 9:1 ratio of CTAB and IGEPAL 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl	27
4.15.	Relation between inverse of surface tension and $\cos \theta$ for 9:1 ratio of CTAB and IGEPAL 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl	28
4.16.	Change in interfacial tension for 9:1 ratio of CTAB and IGEPAL 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl	28
4.17.	Relation between interfacial tension and surface tension for 9:1 ratio of CTAB and IGEPAL 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl	29
	Change in work of adhesion for 9:1 ratio of CTAB and IGEPAL 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl with change in $\log C$	

List of tables

Table no.	Title	Page no.
2.1.	Previous studies on mixed surfactant system	9
4.1.	Surface excess and minimum surface area values	16
4.2.	Value of interaction parameter for different micellar mole fractions of IGEPAL 630	19
5.1.	Minimum contact angle and surface tension achieved ts	31

List of symbols

Greek symbols

γ - Surface tension

τ - Surface excess

θ - Contact angle

English symbols

A_{\min} - Minimum surface area

A_{\max} - Maximum surface area

W_a - Work of adhesion

INTRODUCTION

1. Importance of wetting

Wetting of solid surfaces has been a topic of immense interest since last few decades keeping in view of the wide ranges of applications. It refers to a phenomenon involving spreading of a liquid layer on a solid surface resulting from simultaneous action of interfacial forces between solid, liquid and gas phase. A large number of industrial fields such as froth flotation (Al-Otoom et al., 2009), oil recovery, (Fuerstenau et al., 1991) oil agglomeration (Garcia et al., 1998), solid-liquid separation in wetting medium (Cournil et al., 2006), surface cleaning, dust abatement (Ulusoy and Yekeler, 2004) coating, adhesion, printing and detergency (Neumann and Good, 1979, Adamson, 1991, Janczuk et al., 1999) demand a basic understanding of the wetting process, and the parameters affecting process. If wetting and dewetting properties of surfaces are known, then van der Waals interactions, interfacial free energy, spreading and capillary flow phenomena can be easily explained. (Xia et al., 2001).

1.1. Wetting of a solid surface

Wettability of a solid surface is quantitatively measured in terms of contact angle. Contact angle is the angle between the solid-liquid and liquid-air interface. When contact angle is 180° , the surface is said to have zero affinity towards the liquid or non wetting. When the angle is 0° , the surface is said to have the affinity towards that liquid or complete wetting of the surface by the liquid. Both of these are the extreme cases, whereas in the actual cases, the contact angle between a solid and liquid varies between 0° and 180° .

During spreading process the liquid molecules are arranged on the solid surface so as to minimize the entropy and make the system stable. So while forming a drop of a liquid, the free energy of the molecules exposed on the liquid air interface is actually the minimum possible amount of energy of the corresponding system of solid and liquid.

The solid surfaces are broadly categorized as hydrophobic or hydrophilic depending upon the extent to which the wetting of the surface is facilitated.

As the name itself implies, hydrophilic surface means surfaces having affinity to water.. Since contact angle is less, the exposed area of liquid to air is less. Water spreads very well on these surfaces giving a contact angle less than 90° . Glass is an example of this type of surfaces.

On the other hand, on hydrophobic surfaces, water does not spread well. The water drops formed on these surfaces have higher surface energy because of higher surface area. Contact angle formed is always more than 90° .

1.2. Effect of surfactants on wettability

As illustrated before, quite a good number of applications are there so far as wetting of a solid is concerned. Wettability enhancement of hydrophobic surfaces as per our requirement is possible using aqueous solution of various surface active agents with reference to pure water. When surfactant molecules are introduced to the liquid, the surfactant molecules along with the solvent molecules are oriented in a manner so as to minimize the entropy. More is the dissimilarity between structures of surfactant and a solvent molecule more is the tendency to decrease the entropy.

Decreasing the wettability is particularly important in case of those materials which may damage in contact with water, for example, in food industries where food coming in contact with moisture is not desirable, in order to maintain the freshness, reducing wettability is desirable. In painting and coating applications non wetting is desirable. Increasing wettability is important in cases where complete contact of a solid surface with a liquid is desirable. In textile industries, increasing the wettability of fibres is desirable for effective dyeing and cleaning.

1.3. Surfactant adsorption:

A surfactant or surface active agent alters the property of the liquid which affects the wettability of the solid surface for the corresponding liquid. To change the wettability of hydrophobic surfaces, different surfactants are used which get adsorbed at the solid liquid interface.

In case of surfactant adsorption, surfactant molecules get adsorbed on the solid-liquid interface and lower the overall free energy of the system. Adding more and more surfactant molecules to the solvent increases the surfactant concentration at the interface and surface tension goes on decreasing till CMC.

1.3.1. Types of surfactants

The surfactants are broadly classified into cationic, anionic, non-ionic and zwitterionic depending upon the charge of head group attached to the surfactant molecule. When the head group is negatively charged, the surfactant is called anionic and if positively charged it is called cationic surfactant. Head group is neutral in case of non-ionic ones. Zwitterionic

surfactants carry both the charges and behave as cationic, anionic and non-ionic depending upon pH of solvent, temperature, concentration and other conditions.

1.3.2. Mixed surfactant system

Properties surfactants of different or the same type were mixed and their properties were studied extensively. The role of a mixed system of surfactants in enhancing wetting properties was investigated by different investigators. Mixed system of surfactants usually has a critical micelle concentration which may be greater than or less than that of individual ones depending upon the interaction between individual surfactant molecules, the effects being named as antagonism or synergism respectively. In the cases where a lower CMC value is achieved, a more economical way of changing surface properties is provided. The mixed surfactant system is comparatively unexplored area with respect to that of single surfactant.

1.3.3. Application of mixed surfactant system

Industrial application of surfactant mixtures include dispersion/flocculation, flotation, emulsification, corrosion inhibition, cosmetics, drug delivery, chemical mechanical polishing, enhanced oil recovery (Zhang and Somasundaran, 2006) industrial cleaning and degreasing of metals surface (Davis et al., 2003). Mixture of surfactants shows better result in improving wetting characteristics than pure ones in most of the practical applications. In fact, the commercial surfactants designated as pure surfactants in some cases are mixtures of surfactants due to nonhomogeneous raw materials, presence of unreacted raw materials or formation of by products. (Zdziennicka et al., 2003).

LITRATURE REVIEW

2.1. Single surfactant system

Broad range of research has been performed on solution behaviour and contact angle studies for single surfactant systems. The effect of SDS concentration on contact angle was studied by Serrano-Saldaña et al. (2004) with an objective to study the effect of ionic strength and surfactant concentration which is given in figure-2.1.

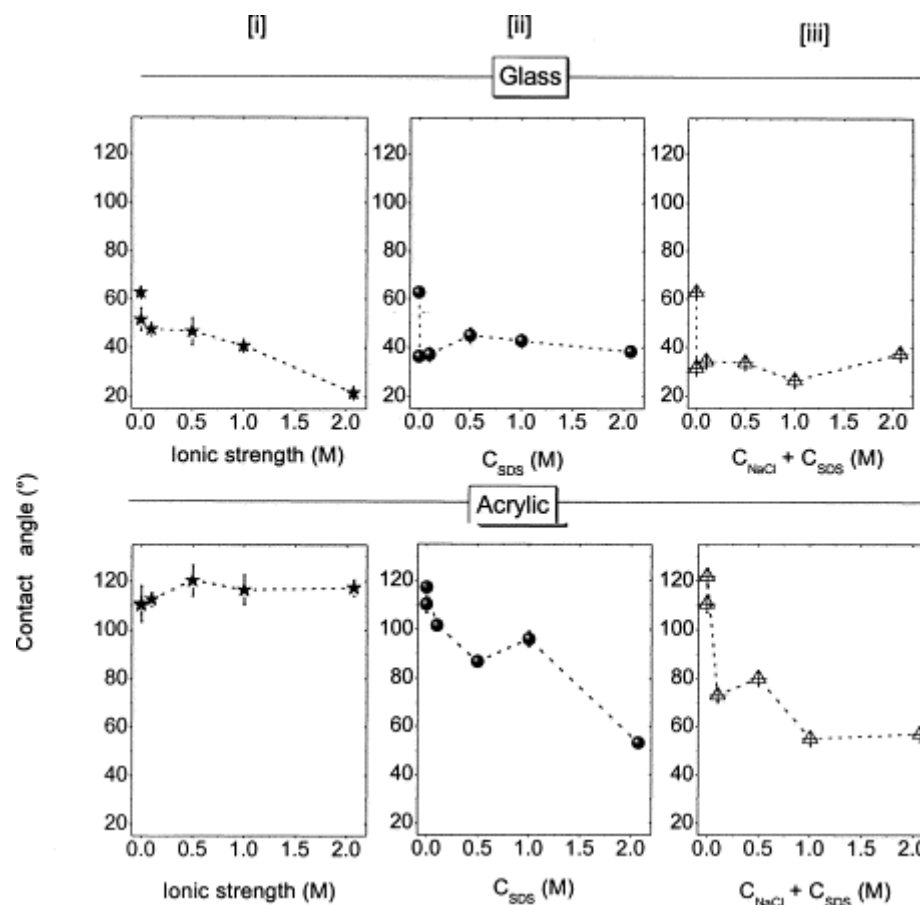


Figure-2.1 Contact angles (θ) of solid/ n -C₁₂/brine systems as a function of: (i) ionic strength; (ii) C_{SDS} ; and (iii) $C_{NaCl} + C_{SDS}$. (Serrano-Saldaña et al., 2004)

Dutschk et al. (2003) studied the wetting behaviour of non-ionic and ionic surfactants on teflon surface and the following trend was found to be followed.

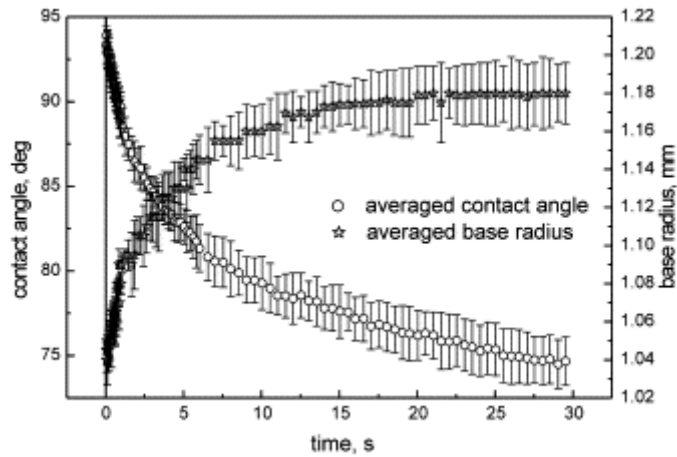


Figure-2.2 Contact angle relationship with time of $C_{12}E_5$ on Teflon AF surface (Dutschk et al., 2003)

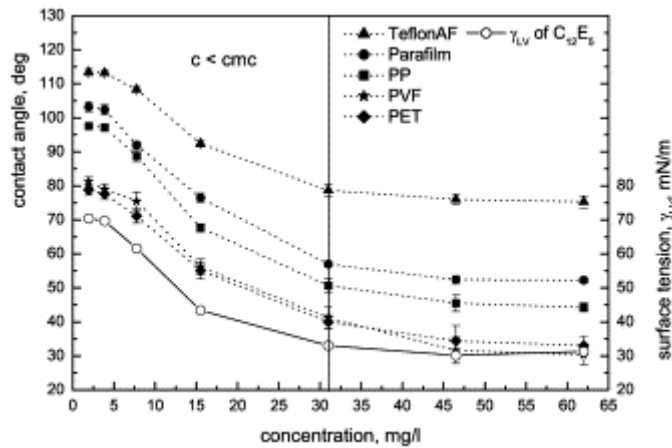


Figure-2.3 Contact angle relationship with concentration of SDS (Dutschk et al., 2003)

In order to analyze the equilibrium state, an algorithm to correct the contact angle taking evaporation into account is presented in this study done by Dutschk et al. (2003).

To establish relation between solution behaviour of single surfactant solutions with concentration, using sodium dodecylsulfate (SDS) and sodium dioctylsulfosuccinate (SDOSS) and a non-ionic surfactant Triton X 100 (TX100) Simončič and Rozman, 2007 produced the experimental results which when plotted followed the trend shown in figure-2.4.

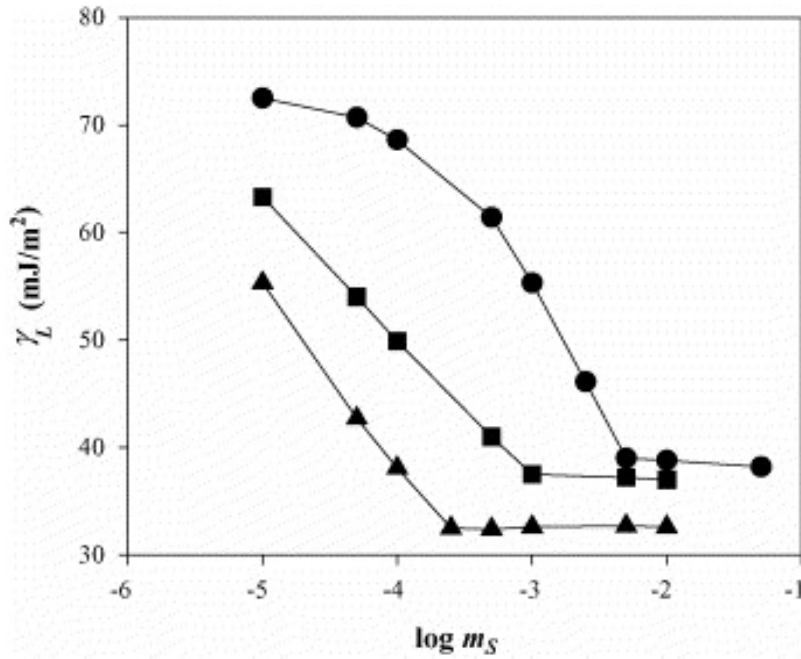


Figure-2.4 Surface tension, γ_L , of surfactant solutions vs. the logarithm of surfactant concentration, $\log m_S$. (●) SDS, (■) SDOSS, (▲) TX100 (Simončič and Rozman, 2007)

The trend followed by surface tension and contact angle due to addition of cationic surfactant on teflon surface was studied by Harkot and Janczuk (2009) which is shown in figure-2.5.

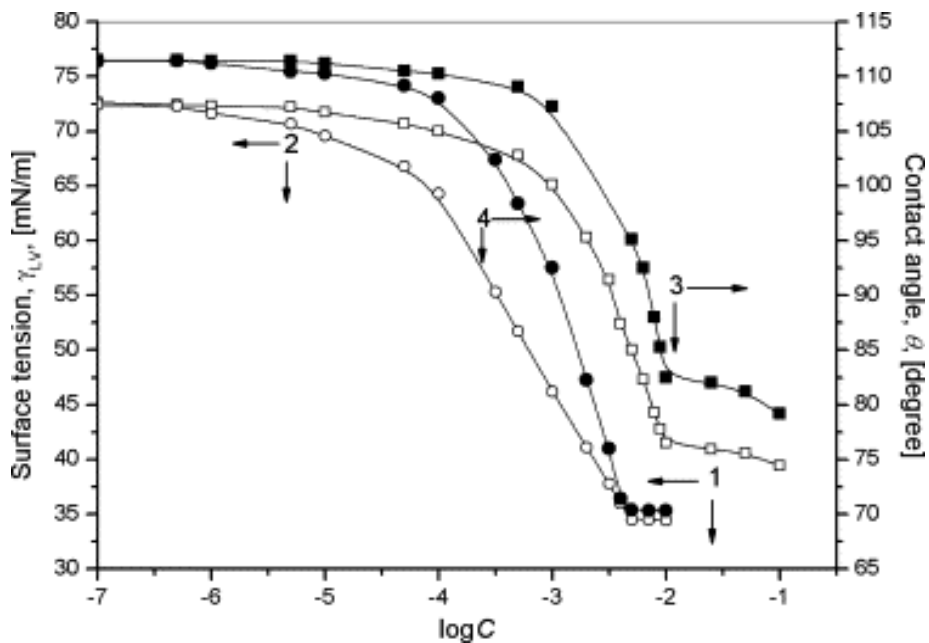


Fig-2.5 The relationship between the values of the surface tension (γ_{LV}) of aqueous C_{12} (EDMAB) (□) and BDDAB (○) solutions and the values of the contact angle (θ) of aqueous C_{12} (EDMAB) (■) and BDDAB (●) solutions for the PTFE surface and the concentration of the surfactants ($\log C$). (Harkot and Janczuk, 2009)

Wetting property of non-ionic surfactants studied by Kim and Hsieh (2001) gave the trend shown in figure-2.6 of varying surface tension with changing concentration of surfactant.

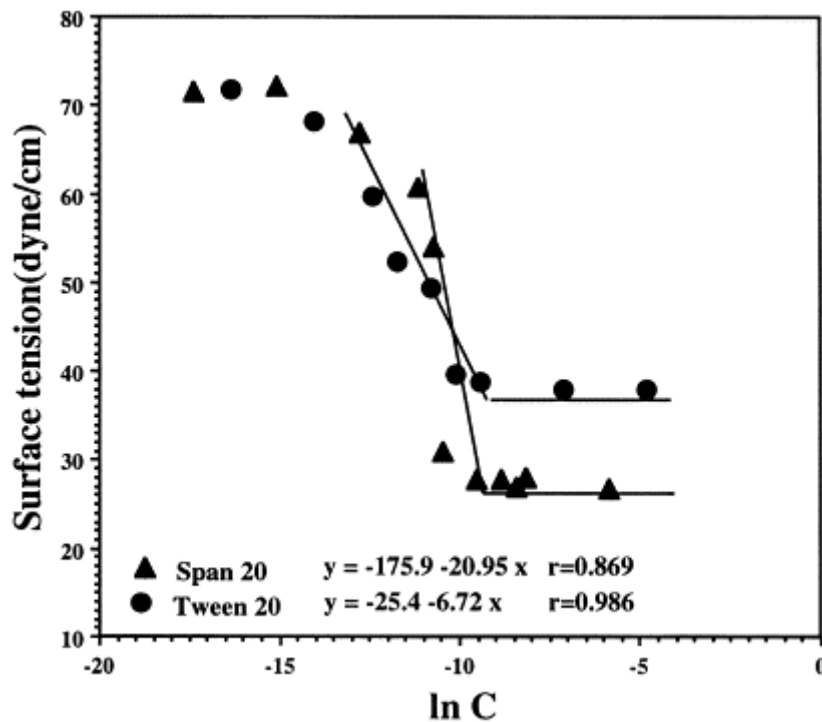


Fig-2.6 Gibbs' adsorption isotherms for Span 20 (▲) and Tween 20 (●). (Kim and Hsieh, 2001)

2.2. Mixture of surfactants

Mixtures of two surfactants showed deviation from the linear dependence between the contact angle and mixture composition, however, no synergism in the wettability was observed. Synergism in the wettability of low-energetic hydrophobic solids should be expected if a mixture of ionic and non-ionic surfactants is added to water. (Rosen, 2004; Gharibi et al., 2000; Li et al., 1998). The works done on mixture of surfactants changing the contact angle can be summarised as given in table no. 2.1

The change in contact angle with mole fraction of a particular surfactant in a mixture of two cationic surfactants is given by Szymczyk et al. (2006) which is presented in figure-2. 7

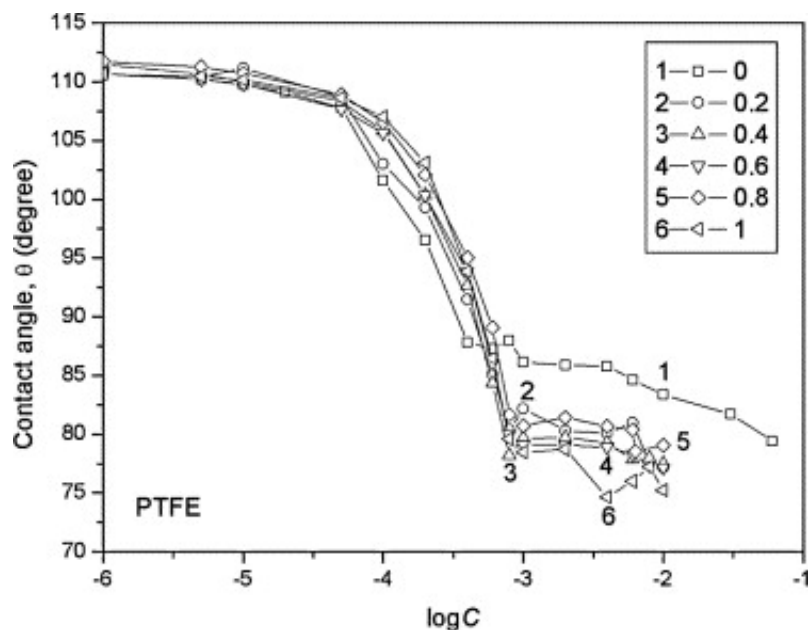


Fig-2.7. The relationship between the contact angle, θ , and $\log C$ (where C is the total concentration of the mixture) for different values of the monomer mole fraction of CTAB, α , in CPyB and CTAB mixture (for PTFE). (Szymczyk et al., 2006)

Similarly the behaviour of a cationic-nonionic mixture was studied by Szymczyk and Janczuk (2006) for which the trend as given in figure-2.8 was followed.

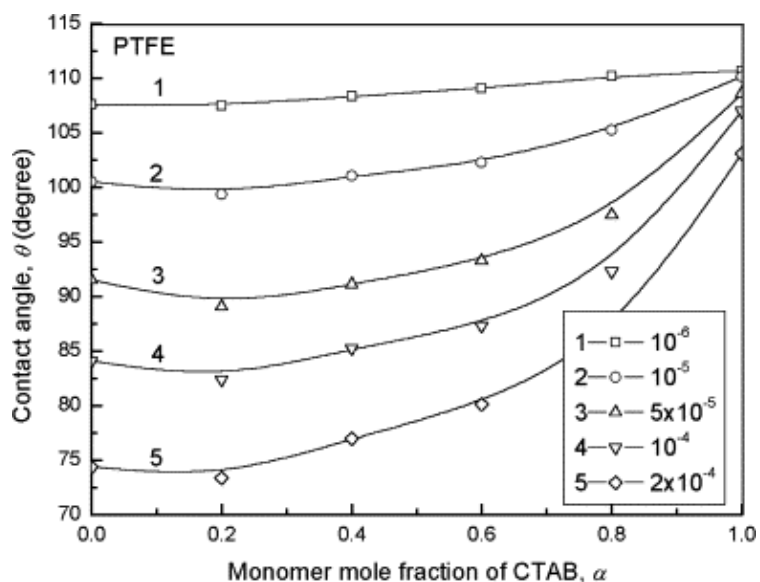


Fig-2.8. The relationship between the contact angle, θ , and monomer mole fraction of CTAB, α , in TX100 and CTAB mixture (for PTFE) at constant total mixture concentration, C , equal to 10^{-6} (curve 1), 10^{-5} (curve 2), 5×10^{-5} (curve 3) 10^{-4} (curve 4) and 2×10^{-4} M (curve 5). (Szymczyk and Janczuk, 2006)

Zdziennicka et al. (2003) studied wettability of polytetrafluoroethylene by aqueous solutions of two anionic surfactant mixtures and the relationship between contact angle with $\log C$ was plotted for different ratios.

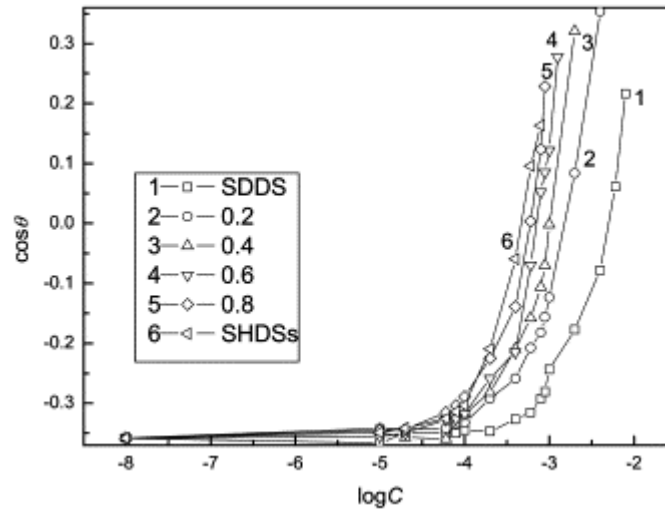


Fig-2.9 the relationship between $\cos\theta$ (θ —contact angle) and logarithm C for different values of the mole fraction (α) of SHDSs in SDS+SHDSs mixture (Zdziennicka et al., 2003)

Table 2.1 Previous studies on mixed surfactant system

Sl no	Combination used	Surfactants used	Surface used	Reference
1	Anionic+Anionic	Sodium dodecyl sulfate and Sodium hexadecyl sulfonate	PTFE	Zdziennicka et al., 2003
2	Cationic+Cationic	Dodecylethyltrimethylammonium bromide and Benzyltrimethylammonium bromide	PTFE and PMMAe	Harkot and Janczuk, 2009
3	Cationic+Cationic	Cetyltrimethylammonium bromide and Cetylpyridinium bromide	PTFE and PMMAe	Szymczyk et al., 2006
4	Non-ionic + Non-ionic	Triton X-100 and Triton X-165	Glass	Szymczyk and Janczuk, 2008
5	Nonionic+Nonionic	Triton X-100 and Triton X-165	PTFE	Szymczyk and Janczuk, 2007
6	Nonionic+Cationic	Triton X-100 and Cetyl trimethylammoniumbromide	PTFE	Szymczyk and Janczuk, 2006
7	Cationic+Anionic	n-dodecyl trimethylammonium chloride, n-dodecyl trimethylammonium bromide, sodium 1-decanesulfonate and sodium dodecyl sulfate	Polyethylene (PE)	Wu and Rosen, 2005

2.3. Effects of additives

In many industrial applications additives are used along with surfactants to improve wetting property. Presence of additives greatly influences various wetting parameters thus providing a more effective way of achieving the desired wettability. Mostly the additives used include alcohols and electrolytes.

2.3.1. Effect of Alcohols

Great deal of research done by Rosen (2004), Zana (1995), Forland et al. (1994), Forland et al. (1998), Attwood et al. (1994), Zana et al. (1981), Rao and Ruckenstein (1986), Castedo et al. (1997) and Leung and Shah (1986) have been presented on the solution behaviour of alcohol and surfactant mixture in changing wetting characteristics. The change of contact angle with concentration of alcohol was presented by Zdziennicka and Janczuk (2008) which is shown in figure-2.10

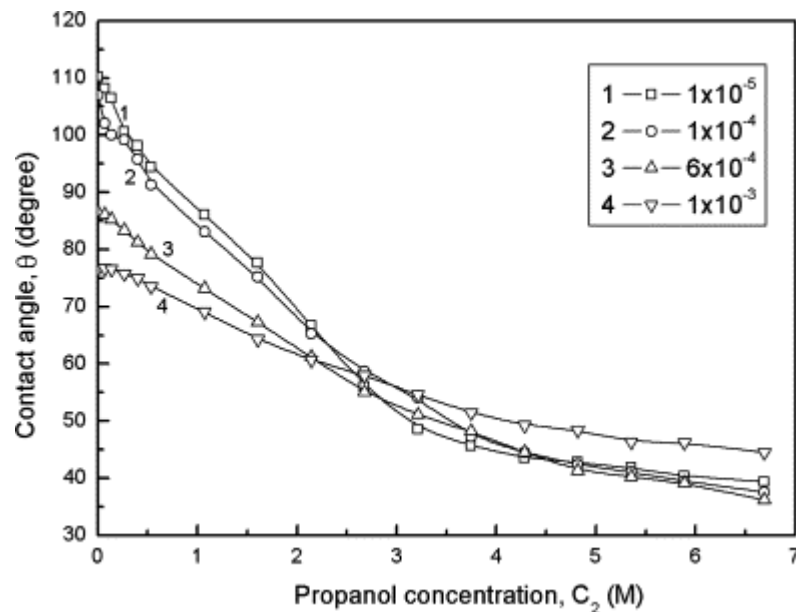


Fig-2.10 Dependence between the measured values of the contact angle (θ) and the propanol concentration. Curves 1, 2, 3 and 4 correspond to the constant values of CTAB equal to 1×10^{-5} , 1×10^{-4} , 6×10^{-4} and 1×10^{-3} M, respectively. (Zdziennicka and Janczuk, 2008)

The solution property observed by alcohol surfactant mixture as given by Tomi et al. (2009) is presented in figure-2.11. the change of CMC with concentration of alcohol can be noticed.

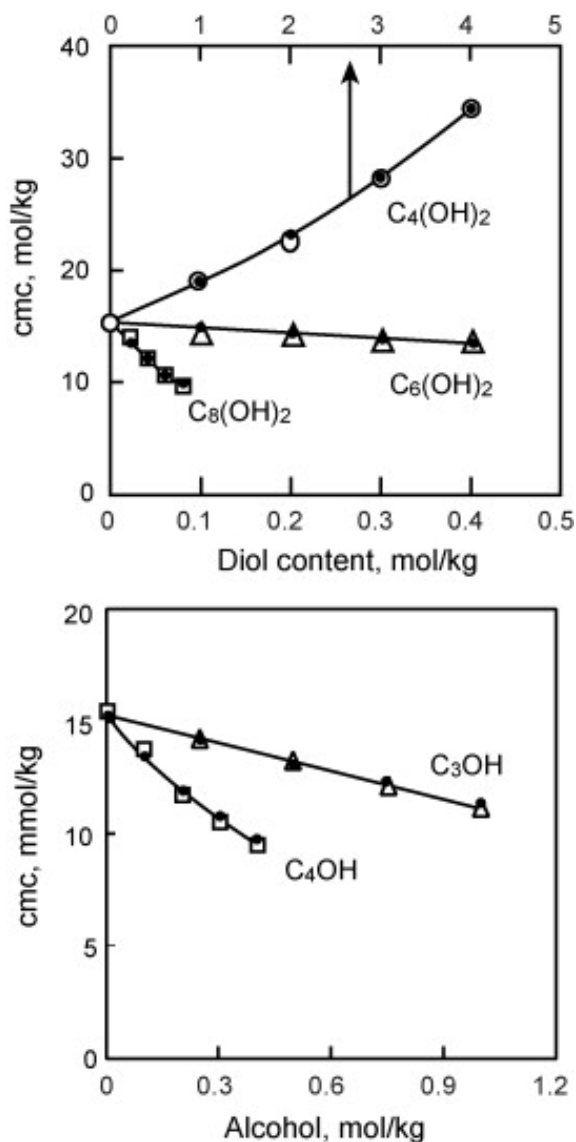


Figure-2.11 Dependence of cmc of DTAB solutions on alcohol content. Open marks denote the experimental results and solid marks denote the calculated values (Tomi et al.)

2.3.2 Effect of electrolytes

The application of electrolytes as additives has been also studied recently. When we add electrolyte to a particular ionic surfactant solution it has been observed that surface tension and contact angle values are reduced. This happens because presence of electrolyte decreases the repulsion between the head groups. As the repulsion is decreased, the CMC is decreased. So the addition of electrolyte can give a more economical way of using the surfactants for decreasing the contact angle and altering the wetting property. (Chaudhuri and Paria, 2009)

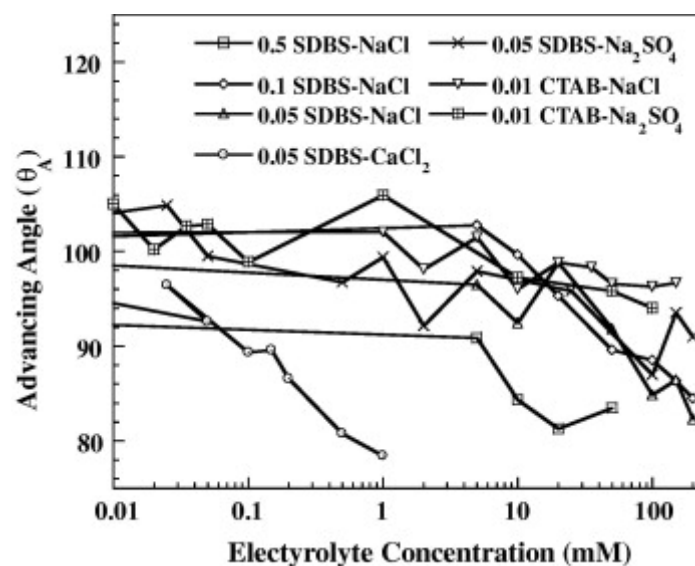


Figure 2.12. Plot of advancing contact angle (θ_A) for different electrolytes (NaCl, CaCl₂, Na₂SO₄) in the presence of SDBS and CTAB solution on the Teflon surface. (Chaudhuri and Paria, 2009)

The above graph was obtained by Chadhuri and Paria (2009) for effect of electrolyte on contact angle of pure surfactants. Dependence of contact angle on concentration and valence of electrolyte is shown in the graph.

EXPERIMENTAL WORK

3.1. Materials

The surfactants used were Igepal- 630 (molecular weight 617gm/mole from Sigma Aldrich, catalogue no-542334) and CTAB (molecular weight 364.46gm/mole from Fluka analytical of 99% purity). Electrolyte used was NaCl with 99.9% purity taken from Ranbaxy Fine Chemicals Ltd. No further purification technique was adopted for surfactants or electrolytes.

3.2. Methods

For measuring surface tension a surface tensiometer, Data Physics, Germany (DCAT-11EC) was used. Platinum sheet is used for surface tension measurement in Wilhelmy plate technique. Three readings for a particular solution were taken and for the final calculations, the average of the three is taken. To avoid the adsorption of surfactant on the plate it was cleaned properly with water and acetone and was also burned to ensure a clean surface. During the experiment, the temperature was maintained constant at a 25⁰c with the help of a circulator.



Figure-3.1: Photograph of Surface tensiometer

For measuring contact angle, contact angle meter, Data Physics, Germany (OCA30) was used. Goniometric technique is used to calculate the contact angle. In Hamilton syringe solution is taken and forced out drop wise with droplets of a fixed volume which can be

adjusted with help of software. Pressing of the piston are movement of the base plate are also done by the instrument itself.



Figure-3.2: Photograph of video based optical contact angle meter

The teflon sheets used for the experimental work were available in form of rolled sheets due to which even a very small portion of a sheet was not found to be completely straight which could lead to deviation in contact angle results. So to avoid the problem, an arrangement of holding the sheet very tightly with help of a base plate and four screws was made. To avoid adsorption of surfactant on the surface teflon sheet is washed with water acetone and Chromic acid

RESULT AND DISCUSSION

4.1. Solution behaviour of pure surfactants

Surface tension measurements were done for different concentrations of both the cationic and non-ionic single surfactants to get the CMCs as well as minimum surface tension values. Apart from the CMC values minimum surface tension is also very important in any interfacial phenomena. The surface tension values obtained were plotted against $\log C$ in Figure 4.1. From the figure it is very clear that the CMC value of Igepal-630 is much lower than CTAB with a lower minimum surface tension value. Then, quantitatively to get an idea about the adsorption of surfactants at the air-water interface, Gibb's surface excess equation is used to calculate the surface excess values as well as minimum surface area occupied per molecule (Chaudhuri and Paria, 2009):

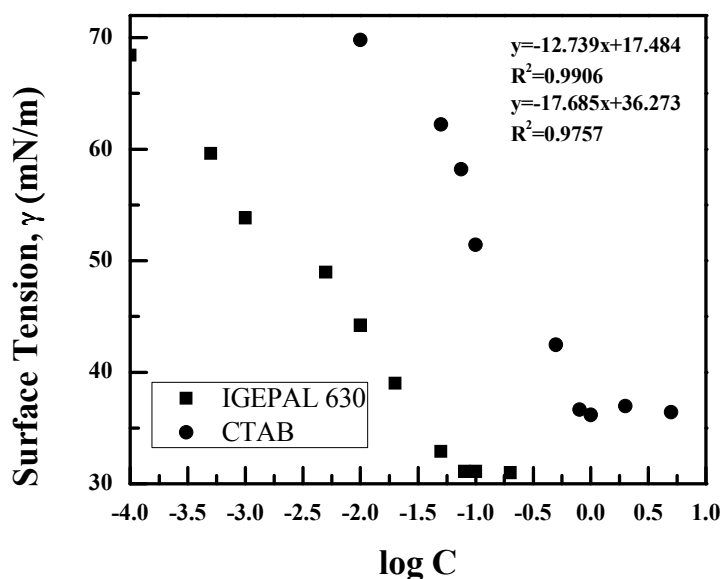


Figure- 4.1: Change of surface tension with $\log C$ for CTAB and Igepal-630

$$\Gamma = -\frac{1}{n \times 2.303RT} \frac{d\gamma}{d \log C} \quad (4.1)$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad (4.2)$$

where Γ is the surface excess in mole/m², A_{min} is surface area per molecule in nm², R is universal gas constant (8314 m³ Pa/kg mole K), T is absolute temperature, and N_A is

Avogadro number (6.023×10^{23}). The value of surface excess and A_{min} are calculated from the experimental data given in table 4.1

Table-4.1: surface excess and minimum surface area values

Surfactant	CMC (mM)	γ_{CMC} (mN/m)	Exp. Γ_{max} (mole/m ²) $\times 10^6$	Exp. A_{mi} (nm ²)	Lit. Γ_{max} (mole/m ²) $\times 10^6$	Lit. A_{min} (nm ²)
CTAB	0.8	31.1	1.55	1.072	1.8 (at 30 °C) (Rosen, 2004)	0.91 (Rosen, 2004)
Igepal-630	0.08	36.6	2.23	0.744		

The value obtained experimentally was close to the value obtained from literature, the small difference with the reported value may be due to the difference in temperature of 5°C, as higher temperature adsorption density decreases, and finally resulting in higher A_{min} . From A_{min} we can get an idea about the packing of surfactant molecules at the air-liquid interface. A_{min} is lower in the case of Igepal-630 which implies more adsorption density than CTAB being a non-ionic surfactant.

4.2 Wetting behaviour of pure surfactants

After studying the solution behaviour wettability of two pure surfactants was studied. Figure 4.2 shows change in contact angle on PTFE surface with the change in surfactant concentration at the aqueous solution.

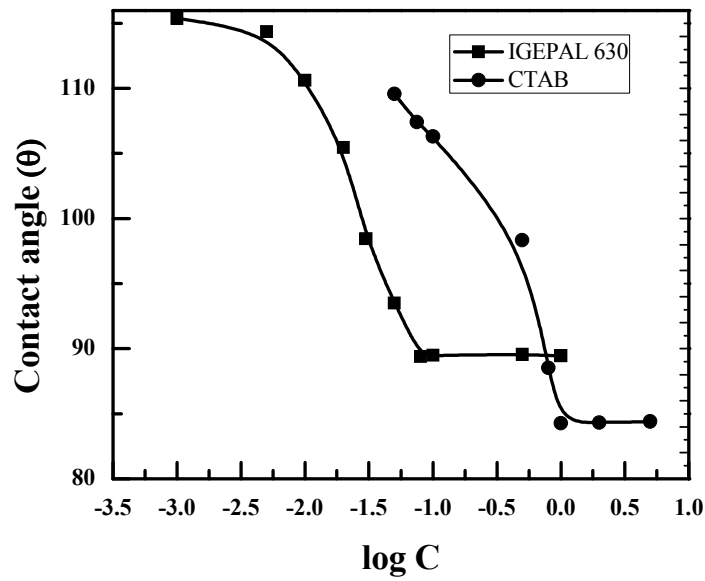


Figure-4.2 Change in contact angle with change in log C for CTAB and Igepal-630

A relationship considering Young and Gibbs equation gives the equation

$$\frac{d(\gamma_{LV} \cos \theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \quad (4.3)$$

Taking $\Gamma_{SV} = 0$, from the equation (4.3) it can be explained that the graph between surface tension and adhesional tension also gives the ratio between surface excess of solid-liquid and liquid-air interface.

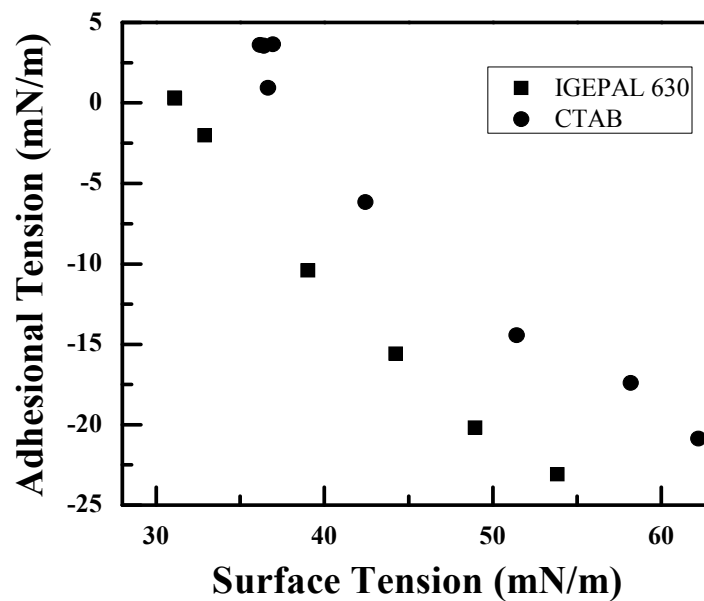


Figure-4.3 Variation of adhesional tension with surface tension for CTAB and Igepal-630

From figure-4.3, the slope is -1.0731 for Igepal- 630 which on putting in equation (7), the value of $\Gamma_{SL} = 2.3958 \times 10^{-6}$ (mole/m²) while for CTAB the slope is -1.003 and $\Gamma_{SL} = 1.554 \times 10^{-6}$ (mole/m²) which implies adsorption density is more for Igepal- 630 on solid-liquid interface than CTAB. There is no equal adsorption at solid-liquid and liquid-air interface which is evident from Γ_{SL} and Γ_{LV} values.

4.3. Solution behaviour of the mixed surfactant system

According to Rubingh's regular solution theory for mixed micelles, the mixed CMC (C_{12}) for system obtained by mixing two surfactants is given by the Eq. (4.4) (Rubingh, 1979),

$$\frac{1}{C_{12}} = \frac{\alpha_1}{f_1 C_1} + \frac{(1-\alpha_1)}{f_2 C_2} \quad (4.4)$$

where C_1 and C_2 are the CMC of first and second individual surfactant, C_{12} is that of the mixture, f_1 and f_2 are the activity coefficients value of which are taken as 1 in case of ideal behaviour. Thus assuming ideal behaviour, equation (4.4) becomes

$$\frac{1}{C_{12}} = \frac{\alpha_1}{C_1} + \frac{(1-\alpha_1)}{C_2} \quad (4.5)$$

For different values of α_1 the experimentally found CMC and mathematically calculated CMC from equation (4.5) are plotted in figure-4.4. The deviation of experimental value from the calculated value shows the deviation of the solution from ideal behaviour.

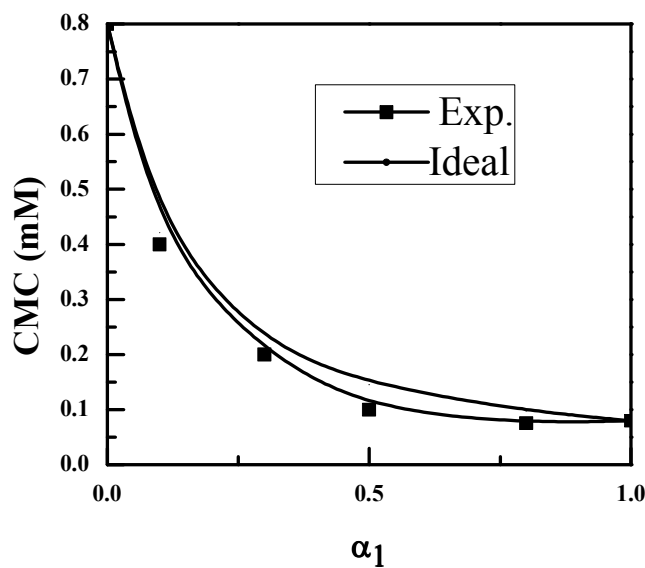


Figure -4.4. Variation of CMC of mixed surfactant system with varying micellar mole fraction

To get a quantitative idea about deviation from ideal behaviour as a result of interaction between two surfactants, interaction parameter β is defined. Rubingh defined a relation

$$\frac{(x_1)^2 \ln \left[\frac{\alpha_1 C_{12}}{x_1 C_1} \right]}{(1-x_1)^2 \ln \left[\frac{(1-\alpha_1) C_{12}}{(1-x_1) C_2} \right]} = 1 \quad (4.6)$$

Using the value of x_1 from equation (4.6), β is calculated

$$\beta = \frac{\ln \left(\frac{\alpha_1 \times C_1}{x_1 \times C_1} \right)}{(1-x_1)^2} \quad (4.7)$$

From the relations given in equation (4.6) and (4.7) β value is calculated for the four mixtures with different ratios which are given in table 4.2.

Table 4.2 (value of interaction parameter for different micellar mole fractions of Igepal-630)

C_1	C_2	C_{12}	X_1	β	α_1
0.08	0.8	0.4	0.52	-0.206	0.1
0.08	0.8	0.2	0.77	-0.469	0.3
0.08	0.8	0.1	0.74	-2.576	0.5
0.08	0.8	0.075	0.83	-3.253	0.8

Value of β is becoming more and more negative showing negative deviation increasing with mole fraction of Igepal- 630. These theoretical values support the graphical inferences drawn from figure 4.3, thus confirming and giving a quantitative measure of nonideality of the mixture.

4.4. Wettability of mixed surfactant system

The measured values of the $\cos \theta$ for aqueous solution of Igepal-630 and CTAB mixtures on the PTFE surface is presented in figure 4.5. The figure shows the dependence of $\cos \theta$ on $\log C$ for different ratios of concentration of Igepal-630 and CTAB. It is observed in the graph that with increase in $\log C$ from -3 to -0.5 (9:1), from -3 to -0.25 (7:3), from -3 to -0.75 (1:1) and from -3 to -1.20 (1:4) θ decreases and then becomes constant for any further increase in value of $\log C$. Change in contact angle is maximum in the lower concentration region. The maximum changes of the contact angle occurring in the concentration range of solutions correspond to the increase of surfactant monomer concentration with surfactant addition to the liquid. The region where with increase in concentration no further decrease of contact

angle is observed is the region corresponding to formation of micelles and increasing concentration in micelle.

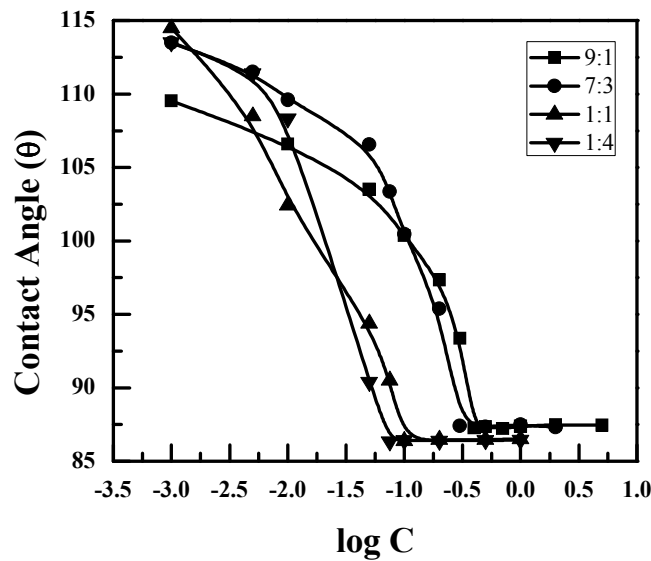


Figure 4.5 change of contact angle θ with respect to changing concentration C of surfactant.

The measured values of the $\cos CA (\theta)$ for aqueous solution of Igepal- 630 and CTAB mixtures on the PTFE surface is presented in figure 4.5. The figure shows the dependence of $\cos \theta$ on $\log C$ for different ratios of concentration of Igepal- 630 and CTAB. It is observed in the graph that with increase in $\log C$ from -3 to -0.5 (9:1), from -3 to -0.25 (7:3), from -3 to -0.75 (1:1) and from -3 to -1.20 (1:4) θ decreases and then becomes constant for any further increase in value of $\log C$. Change in contact angle is maximum in the lower concentration region. The maximum changes of the contact angle occurring in the concentration range of solutions correspond to the increase of surfactant monomer concentration with surfactant addition to the liquid. The region where with increase in concentration no further decrease of contact angle is observed is the region corresponding to formation of micelles and increasing concentration in micelle.

4.4.1. Adsorption at solid-liquid and liquid-air interface

According to Bargeman et al., 1973 that there is a linear relationship between the adhesion tension and surface tension of aqueous solutions of surfactants ($\gamma_{LV} \cos \theta = a \gamma_{LV} + b$; a and b are constants) both for individual surfactants and also for mixtures. But for all the ratios value of a and b in linear equations were near the same for a given polymeric solid. So to describe the relation between adhesional tension and surface tension on teflon surface we have (Szymczyk et al., 2005),

$$\gamma_{LV} \cos \theta = -\gamma_{LV} + 46.88 \quad (4.8)$$

using the relationship between adhesional tension and surface tension the relation between surface free excess at solid-liquid and liquid-air interface can be obtained as in case of pure surfactants from equation (4.3)

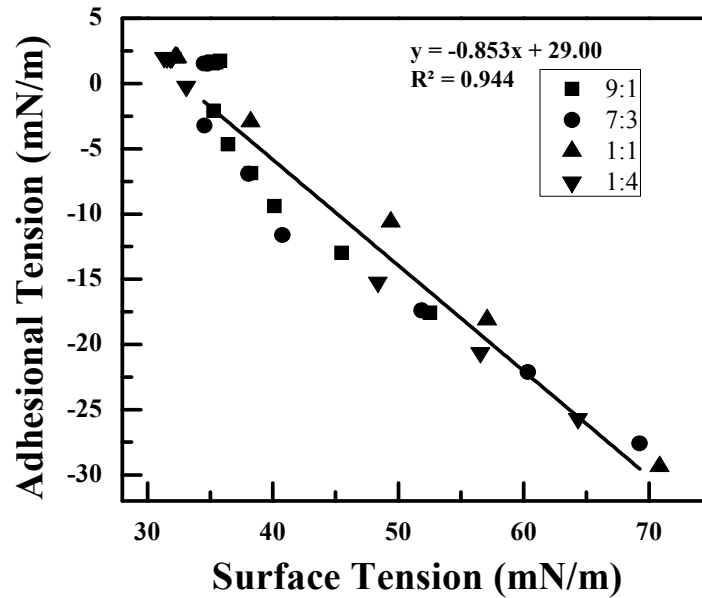


Figure 4.6. Variation of adhesional tension with varying surface tension

The relationship between the values of $\gamma_{LV} \cos \theta$ and the surface tension (γ_{LV}) of aqueous solution of Igepal- 630 and CTAB mixture on PTFE are shown in the above figure.

Extrapolating the straight linear dependence given by equation (4.8) to the point where $\cos \theta=1$, i.e $\theta=0$, γ_c can be calculated, the liquid surface tension required to give zero degree contact angles, which is known as critical surface tension. (Szymczyk et al., 2006)

In figure 4.7, the relation between γ^{-1} and $\cos \theta$ is observed. In this plot if we extrapolate the graph to the point at which value of $\cos \theta$ is equal to 1, the corresponding value of surface tension will give critical surface tension. Critical surface tension is the surface tension value at which complete wetting of a solid surface is there i.e. $\theta=0$.

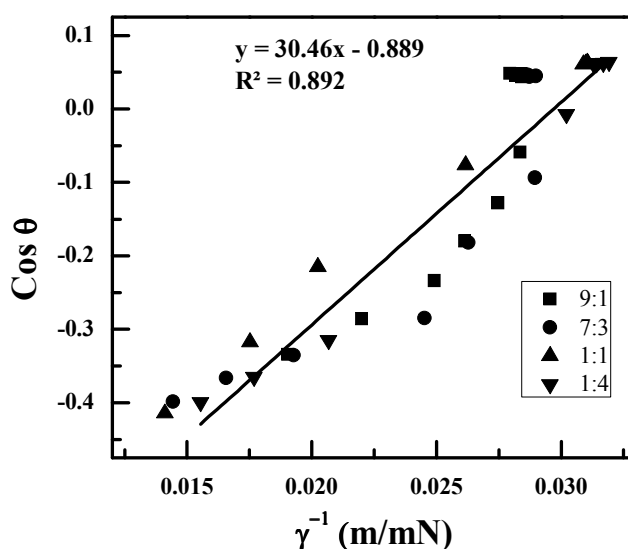


Figure- 4.7 relationship between inverse of surface tension with $\cos \theta$

4.4.2. Critical surface tension

From Young's equation $\gamma_{SV} - \gamma_{SL} = \lambda_{LV} \cos \theta$ (4.9)

It is possible to calculate the solid-solution interfacial tension from Eq. (4.9) on the assumption that both $\gamma_{SV} = \gamma_S \neq \gamma_C$ and $\gamma_{SV} = \gamma_C$. For calculation of the values of aqueous solutions of Igepal- 630 and CTAB mixtures, the surface tension of PTFE (20.34 mN/m) was taken. For different ratios of concentration of CTAB and Igepal- 630, the change of interfacial tension with Log C is shown in figure 4.4. Rapid decrease in interfacial tension is observed in between the range -3 to -1 or -0.5 and then it becomes constant for anymore increase in Log C. There is also a decrease in the value of Log C at which saturation is reached for the four ratios with the increase in percentage of Igepal- 630 in the mixture.

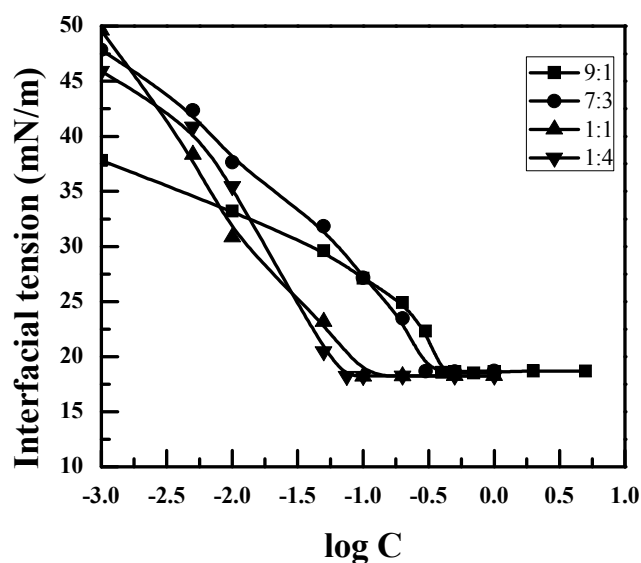


Figure-4.8 Change in interfacial tension with change in log C thus determining critical surface tension

4.4.3. Linearity of relation between surface tension and interfacial tension

In figure-4.9 linear relationship between surface tension and interfacial tension is shown. Interfacial tension increases with increase in surface tension which again implies an inverse relationship between concentrations of surfactant. It can also be observed that the slope or the intercept does not change much with the four ratios. So this relationship is not dependent upon the micellar mole fraction α .

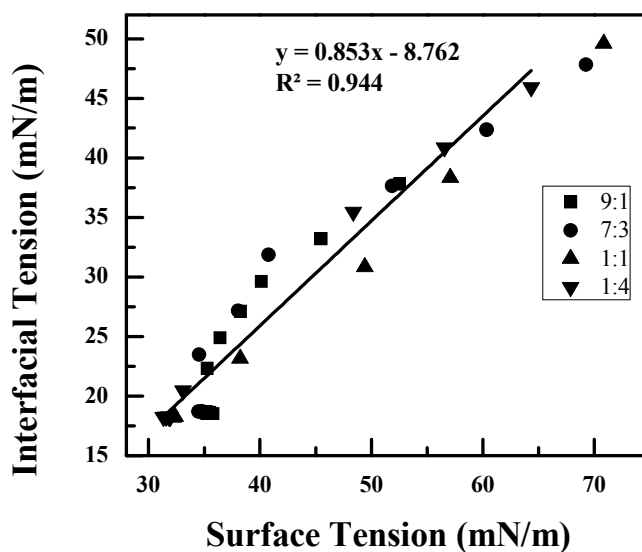


Figure-4.9 linear relation between surface tension and interfacial tension

4.4.4. Work of adhesion on Teflon surface

Dependence between the adhesion work (W_A) of the aqueous solutions of surfactants to PTFE surface and $\log C$ is shown in figure – 4.6. The solid–solution interfacial tension fulfils the condition

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - W_A \quad (4.10)$$

where W_A is the work of adhesion of the liquid to solid surface, which can be treated as the sum of two components, apolar (Lifshitz–van derWaals), $W_A(\text{apolar})$, and polar, $W_A(\text{polar})$, interactions across solid–liquid interface. (Szymczyk et al., 2006)

Using Young’s equation another relation can be established as

$$W_A = \gamma_{LV} (\cos \theta + 1) \quad (4.11).$$

This work of adhesion calculated from equation (4.11) is plotted against $\log C$ in figure-4.10. The observed change implies that work of adhesion decreases and then attains a saturation value with increase in $\log C$ for the ratio 1:1 and 1:4 for concentration of CTAB and IGEPAL- 630. But for ratios 9:1 and 7:3 for these two surfactants, work of adhesion decreases, increases a bit and then becomes constant which may be because of predominant effect of non-ionic surfactant in the former two ratios which was not there in the later two ratios.

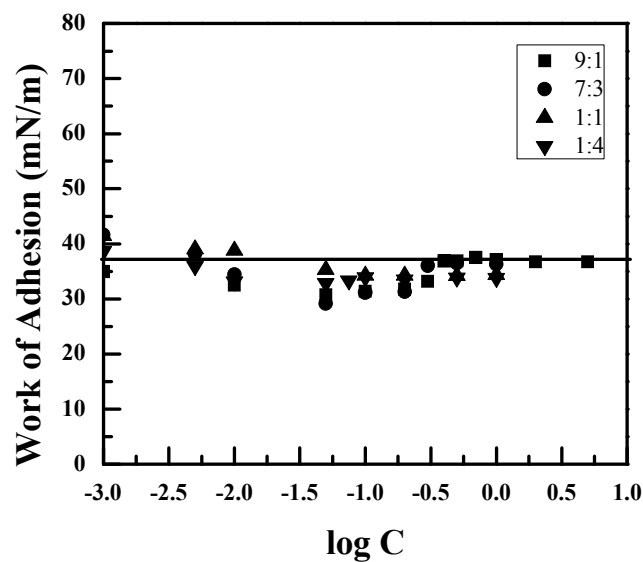


Figure – 4.10 Change of work of adhesion with concentration

4.5. Electrolyte effect on mixed surfactant system

4.5.1. Solution behaviour mixed surfactant system with electrolyte

Effect of presence of electrolyte NaCl in presence of mixed surfactant system with 90% CTAB and 10% Igepal-630 was studied first making surfactant concentration constant and varying electrolyte concentration till saturation value of surface tension and contact angle were achieved and then the same procedure was repeated with two more concentrations of the same surfactant system.

Presence of electrolyte decreases the repulsion between head groups of ionic surfactants and thus improving adhesion and wettability. However, non-ionic surfactants are not much affected by the electrolyte. So the mixture with ratio 9:1 of cationic and non-ionic surfactants respectively was chosen to study the effect of electrolyte.

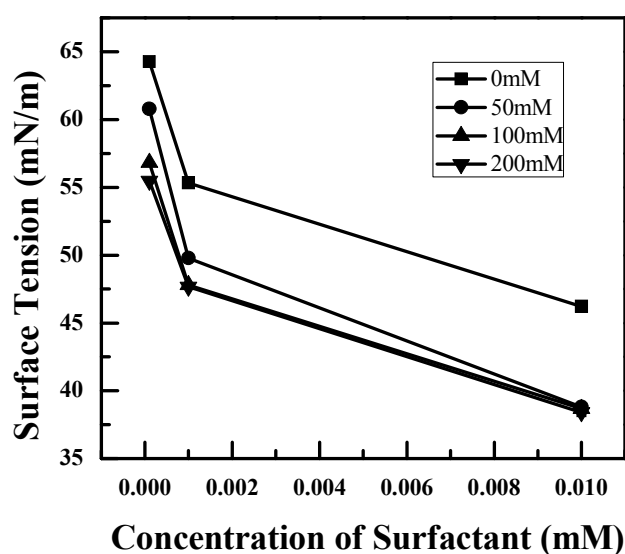


Figure 4.11 change of surface tension with concentration of surfactant for a particular value of concentration of electrolyte

In figure-4.11 change of surface tension with surfactant concentration for four different concentration of electrolyte is plotted. All the four graphs follow the same trend in decreasing the surface tension. But with increasing electrolyte concentration, for the same concentration of surfactant, value of surface tension reduces. This provides an effective way of reducing surfactant consumption. Taking a closer look at the plot also reveals that an addition of 100mM of electrolyte is efficient of reducing consumption of surfactant by approximately 10 times

The difference in surface tension value is more between pure surfactant and 50mM of electrolyte with surfactant. With increasing electrolyte concentration, the difference reduces. This implies that at low salt concentration, electrolyte effect is more and after that, for a

particular surfactant concentration, surface tension attains a saturation value which does not change for any further change in electrolyte concentration.

4.5.2. Wettability of mixed surfactant system with electrolyte

In figure-4.12 the variation of contact angle with concentration of surfactant is shown for four different concentrations of electrolyte. In similar ways as in figure-4.8, the contact angle decreases with increasing concentration of electrolyte at a particular surfactant concentration. The difference between contact angle with addition of electrolyte decreases at higher concentration of surfactant. In fact, after adding 100mM of electrolyte, further increase in electrolyte concentration makes almost no change in contact angle except for at very low concentration of surfactant of the order 0.0001.

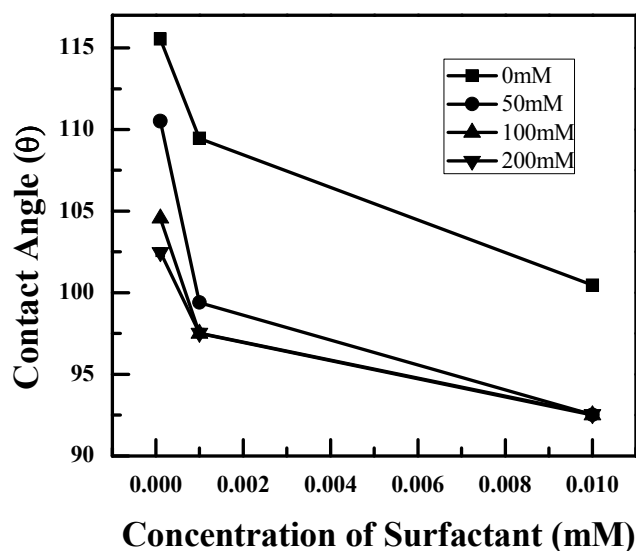


Figure 4.12 Change of contact angle with concentration of surfactant for a particular value of concentration of electrolyte

Now adhesional tension, interfacial tension and work of adhesion are calculated for the mixed surfactant system of CTAB and IGEPAL- 630 in the ratio 9:1 in presence of electrolyte NaCl and the following graphs are plotted.

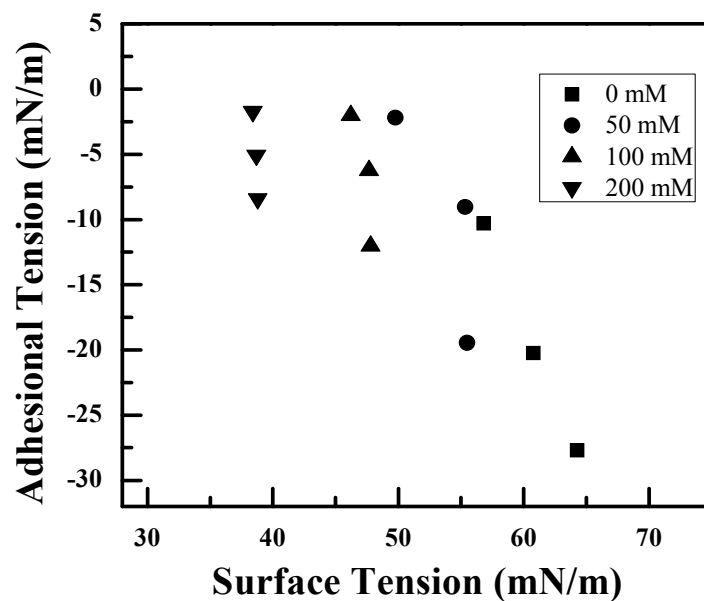


Figure-4.13 change of adhesional tension with surface tension for 9:1 ratio of CTAB and IGEPAL- 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl

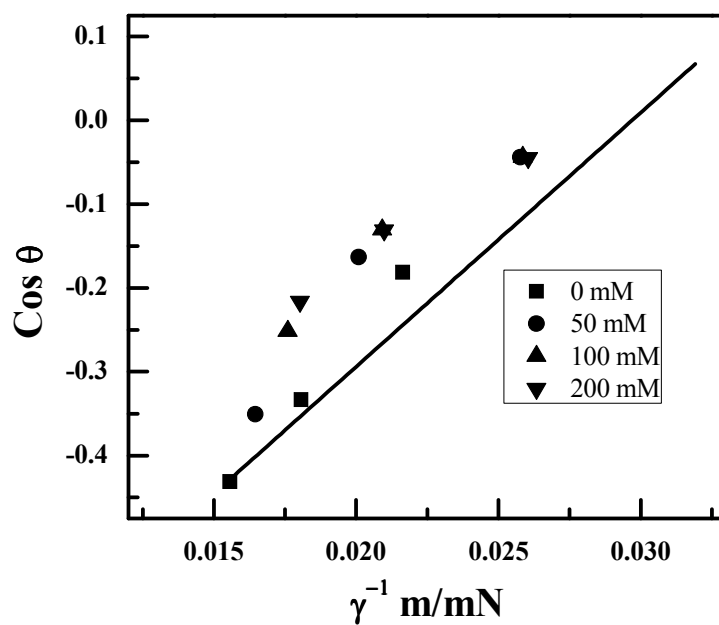


Figure-4.14 Relation between inverse of surface tension and $\cos \theta$ for 9:1 ratio of CTAB and IGEPAL- 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl

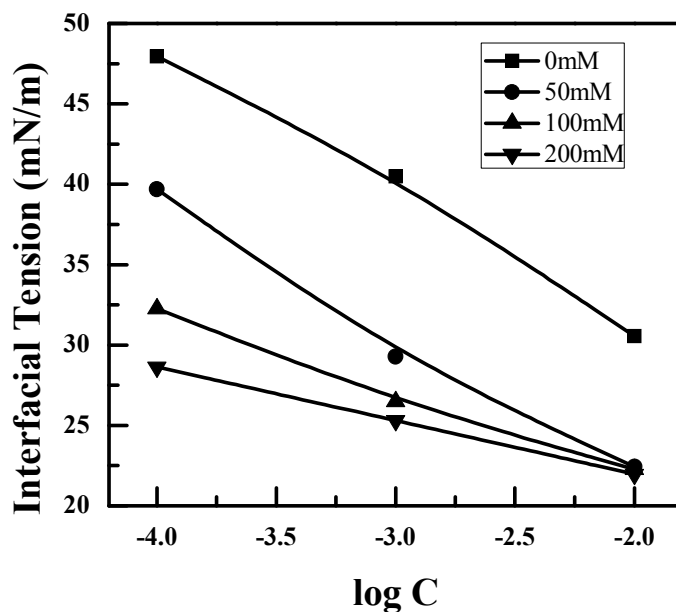


Figure-4.15 Change in interfacial tension for 9:1 ratio of CTAB and IGEPAL- 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl with change in log C

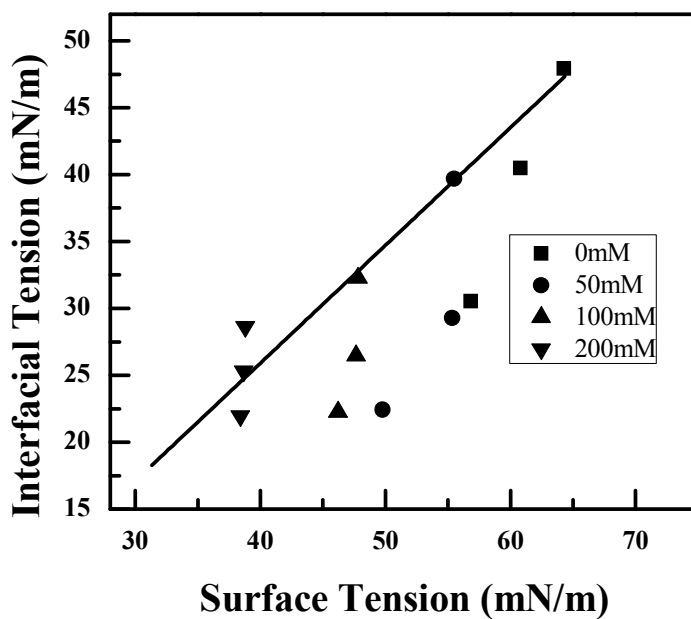


Figure-4.15 Relation between interfacial tension and surface tension for 9:1 ratio of CTAB and IGEPAL- 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl

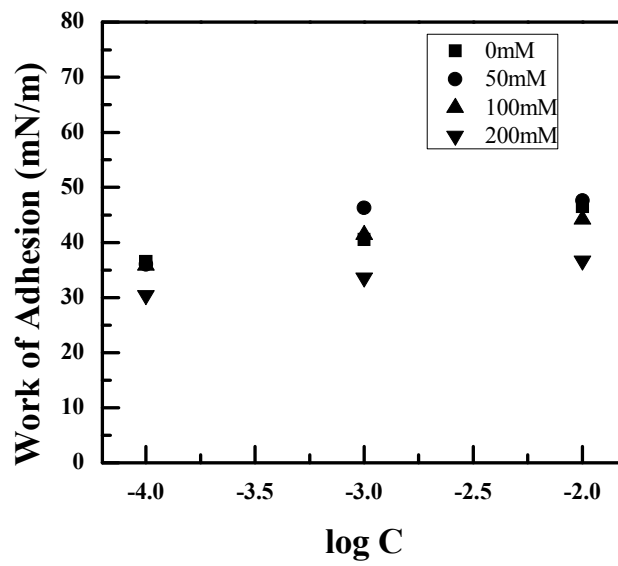


Figure-4.16 Change in work of adhesion for 9:1 ratio of CTAB and IGEPAL- 630 mixed surfactant system with 4 different concentrations of electrolyte NaCl with change in log C

CONCLUSION

- ❖ Increase in $\cos \theta$ value with increase in $\text{Log } C$ and finally attainment of a saturation value.
- ❖ Linear relationship between surface tension and adhesional tension with a negative slope.
- ❖ Inverse of surface tension maintaining linear relation with $\cos \theta$.
- ❖ Decreasing interfacial tension with increasing $\text{Log } C$ and finally reaching saturation value and the value of $\text{Log } C$ corresponding to saturation value decreasing with increase in percentage of IGEPAL- 630 concentration in mixture.
- ❖ Decrease in work of adhesion to a saturation value for higher concentration of non-ionic surfactant
- ❖ Decrease in work of adhesion followed by increase and then finally attaining saturation value for lower concentration of non-ionic surfactant.
- ❖ The nonideality of mixed surfactant system increases with increasing concentration of non-ionic surfactants.
- ❖ Addition of 100mM solution of salt decreases the surface tension and contact angle value of a particular concentration to the surface tension and contact angle corresponding to concentration 10 times the former concentration without electrolyte.

Table-5.1 Minimum contact angle and surface tension achieved

Parameters	CTAB	Igepal-630	CTAB : Igepal--630				CTAB : Igepal--630 = 9:1 (0.01) + NaCl			
			9:1	7:3	1:1	1:4	0	50 mM	100 mM	200 mM
Min. ST	36.65	31.10	35.27	34.	32.	31.33	46.21	38.81	38.67	38.41
CMC (mM)	0.8	0.08	0.3	0.2	0.1	0.075	0.3	0.01	0.01	0.01
Min. θ	84.26	89.4	87.26	87.42	86.38	86.34	100.46	92.43	92.51	92.57

Reported value of minimum contact angle achieved by a system of pure surfactant with electrolyte was 94.25° at 0.01 mM of CTAB with 100 mM of NaCl (Chaudhuri and Paria, 2009), while at a concentration of 0.01 mM in the mixed surfactant system with CTAB and Igepal- 630 in a ratio of 9:1 with 50 mM of NaCl the minimum contact angle obtained was 92.43° . The further step in this project work can be taken as studying the effect of valence of the electrolyte to be added in the mixed surfactant system.

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