PHASE BEHAVIOUR OF L62 AND P104 IN WATER AND BENZYL ALCOHOL MIXTURES AND PHYSICO-CHEMICAL PROPERTIES OF L62, P104 and BRIJ-78 AQUEOUS SOLUTIONS

BY

DANIEL NGISA MOGONCHI

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY, SCHOOL OF SCIENCE, UNIVERSITY OF ELDORET, KENYA.

2013

DECLARATION

Declaration by student

This research thesis is my original work and has not been presented for research study in any other University or Institution. No part of this thesis may be reproduced without prior permission of the author and/or University of Eldoret.

Signature ______________________________ Date

____

DANIEL NGISA MOGONCHI
Sc/PGC/05/02

Declaration by supervisors

This thesis has been submitted for examination with our approval as university supervisors.

Signature.______________________________ Date __________________

Prof. PIUS K. KIPKEMBOI
Department of Chemistry, University of Eldoret,
P.O. BOX 1125, Eldoret.

Signature.______________________________ Date __________________

Dr. M. O. OKOTH
Department of Chemistry, University of Eldoret,
P.O. BOX 1125, Eldoret.

DEDICATION

This research thesis is dedicated to my wife Christine and my children, Marion, Michelle, Sandra Brandon and Obed.

ABSTRACT

The isothermal ternary phase and aggregation behaviour of amphiphilic co-polymer-water-benzyl alcohol systems was investigated for the two non-ionic surfactant systems: L-62 and P104 at 25 ^{0}C. The phase boundaries were examined and identified by visual inspection under polarized light to check for phase separation, homogeneity and birefringency. The microstructures in the lyotropic liquid crystalline phases were determined and characterized by small-angle X-ray scattering (SAXS). Also, Physico-chemical properties of aqueous solutions of Brij-78 [polyoxyethylene (20) Stearly ether ($C_{18}H_{37}(OCH_2CH_2)_nOH$)] and tri-block copolymers L-62 ($(EO)_6(PO)_{34}(EO)_6$) and P104 ($(EO)_{27}(PO)_{61}(EO)_{27}$) non-ionic surfactants were studied. The micellar behaviour of the three surfactants in aqueous media was investigated at 25 ^{0}C. Other thermodynamic and solution properties of aqueous mixtures of the surfactants were investigated with cloud point, conductometric and viscometric techniques. Effects of inorganic salts (NaCl, Na_2SO_4 and $AlCl_3$), ionic surfactants (SDS and CTAB) and nonionic surfactant (TX-114) on the three physico-chemical properties of the surfactant solutions were also determined. A variety of lyotropic liquid crystalline (LLC) phases are thermodynamically stable in the two systems. In the P104-water-benzyl alcohol ternary system, four lyotropic liquid crystalline phases were found to be thermodynamically stable while in the L62-water-benzyl alcohol ternary system, one lyotropic liquid crystalline phase was found to be stable. The copolymer is completely soluble in benzyl alcohol. Cloud point of pure surfactant solutions decreased with increase in surfactant concentrations and inorganic salts: NaCl, Na_2SO_4 and $AlCl_3$ depress cloud points. Ionic surfactants, SDS and CTAB, both raised the cloud point of the three nonionic surfactants to above 100 ^{0}C but TX-114, a nonionic surfactant, lowered cloud point of all three nonionic surfactants. Both specific conductivity and relative viscosity increased slightly with increase in surfactant concentration in all cases. Benzyl alcohol does not produce most lyotropic liquid crystals especially reverse phases and therefore not recommended in cases where such phases are needed.

TABLE OF CONTENTS

DECLARATION..i
DEDICATION ii
ABSTRACT..iii
TABLE OF CONTENTS..iv
LIST OF ABBREVIATIONS x
ACKNOWLEDGEMENT xi

CHAPTER ONE.. 1
INTRODUCTION.. 1
  1.1 Background of the study 1
  1.2 Statement of the Problem..4
  1.3 Study Objectives..5
    1.3.1 Major Research Objective 5
    1.3.2 Specific Research Objectives..5
  1.4 Justification of the Study..5

CHAPTER TWO.. 8
LITERATURE REVIEW 8
  2.1 General Information about the Study..8
  2.2 Classifications of Surfactants 9
    2.2.1 Nonionic Surfactants..10
  2.3 Polymorphism in Surfactants 10
  2.5 Liquid Crystals 12
    2.5.1 Thermotropic Liquid Crystals..13
    2.5.2 Lyotropic Liquid Crystals..14
    2.5.3 Classification and Uses of Lyotropic Liquid Crystals 16
    2.5.4 Uses of thermotropic Liquid Crystals 18
  2.6 Block Copolymers 19
  2.7 Surfactant/water/oil Self-assembly..20
  2.8 Ternary Block Copolymer-water-oil Systems..22
    2.8.1 Phase behavior of block copolymer/water/oil ternary systems 22
    2.8.2 Characterization of Lyotropic Liquid Crystals 24
    2.8.3 Isothermal Ternary Phase Diagrams 26
    2.8.4 Progression of Microstructures in Block Copolymer/water/oil Systems ..29
    2.9.1 Effect of Block Copolymer Molecular Weight on Phase Behavior..........31
    2.9.2 Effect of Block Copolymer Composition on Phase Behavior 33
    2.9.3 Effect of Solvent Quality on Phase Behavior 35
  2.10 Physicochemical Properties of Surfactants 38
    2.10.1 Cloud Point 39
  2.10.4 Determination of CMC 47

CHAPTER THREE.. 48
MATERIALS AND EXPERIMENTAL 48
  3.1 Materials and Sample Preparation..48

3.2 Determination of Phase Behaviour of Ternary Systems: P104/D_2O/Benzyl Alcohol and L62/D_2O/Benzyl Alcohol....49
3.2.1 Sample Preparation 49
3.2.2 Preparation and Identification of Lyotropic Liquid Crystalline Mesophases 49
3.2.3 Construction of Isothermal Ternary Phase Diagrams 50
3.3 Critical Micelle Concentration (CMC) 51
3.4 Cloud Point of the Nonionic Surfactants 52
3.4.1 Procedure for Determination of CP....52
3.4.2 Determination of CP of solutions of L-62, P-104 and Brij-78 52
3.5 Measurement of Specific Conductivity of Solutions of L62, P104 and Brij-78 53
3.6 Measurement of Relative Viscosity....55

CHAPTER FOUR 57
RESULTS AND DISCUSSION 57
4.1 Phase and Structure Behavior of Ternary Systems....57
4.2 Phase Behavior and Structure of P104 and L62 in water and benzyl alcohol. 58
4.2.1 Phase Behavior and Structure of P104/D_2O/Benzyl Alcohol ternary system.... 58
4.2.2 Phase Behavior and Structure of L62/D_2O/Benzyl Alcohol Ternary System.... 64
4.3.1 CP of Aqueous Solutions of L62, P104 and Brij-78.... 70
4.3.2 Effect of Inorganic Salts (NaCl, Na_2SO_4 and $AlCl_3$) on CP of L62, P104 and Brij-78 Aqueous Solutions 72
4 .3.3 Effect of Added Ionic Surfactant (SDS and CTAB) on CP of L62, P104 and Brij-78 Aqueous Solutions.... 75
4.3.4 Effect of Added Non-ionic Surfactant (TX-114) on CP of P104 and Brij-78 Aqueous Solutions 76
4.4 Specific Conductivity of L62, P104 and Brij-78....77
4.4.1 Specific Conductivity of Aqueous Solutions of L62, P104 and Brij-78.......78
4.4.2 Effects of Inorganic Salts (NaCl, Na_2SO_4 and $AlCl_3$) on Specific Conductivity of L62, P104 and Brij-78 80
4.4.3 Effect of Ionic Surfactants (SDS and CTAB) on Specific Conductivity of L62, P104 and Brij-78 Aqueous Solutions.... 84
4.4.4 Effect of Non-ionic Surfactant (TX-114) on Specific Conductivity of L62, P104 and Brij-78 Aqueous Solutions.... 86
4.5 Measurement of Relative Viscosity....87
4.5.1 Relative Viscosity of Aqueous Solutions of L62, P104 and Brij-78....87
4.5.2 Effects of Inorganic Salts (NaCl, Na_2SO_4 and $AlCl_3$) on Relative Viscosity of L62, P104 and Brij-78 90
4.5.3 Effect of Ionic Surfactants (SDS and CTAB) on Relative Viscosity of L62, P104 and Brij-78 Aqueous Solutions.... 92
4.5.4 Effect of Non-ionic Surfactant (TX-114) on Relative Viscosity of L62, P104 and Brij-78 Aqueous Solutions.... 94
4.5.5 Discussion on physic-chemical properties 97

CHAPTER FIVE 100
CONCLUSION AND RECOMMENDATION 100
    5.1 Conclusion 100
    5.2. Recommendation 101
    REFERENCES 102

LIST OF APPENDICES

Appendix I: Cloud point, Specific Conductivity and RelativeViscosity of aqueous solutions of L62 106

Appendix II: Cloud point, specific conductivity and relativeviscosity of solutions of P104 106

Appendix III: Cloud point, specific conductivity and relativeviscosity of solutions of Brij-78 107

Appendix IV: Effect of NaCl on Cloud Point of L-62, P-104 and Brij-78 solutions 107

Appendix V: Effect of Na_2SO_4 on Cloud Point of L-62, P-104 and Brij-78 solutions 108

Appendix VI: Effect of $AlCl_3$ on Cloud Point of L-62, P-104 and Brij-78 solutions 108

Appendix VII: Effect of SDS on Cloud Point of L-62, P-104 and Brij-78 solutions 108

Appendix VIII: Effect of CTAB on Cloud Point of L-62, P-104 and Brij-78 solutions 109

Appendix IX: Effect of TX-114 on Cloud Point of P-104 and Brij-78 solutions. . 109

Appendix X: Effect of NaCl on Specific Conductivity of L-62, P-104 and Brij-78 solutions 110

Appendix XI: Effect of Na_2SO_4 on Specific Conductivity of L-62, P-104 and Brij-78 solutions 110

Appendix XII: Effect of $AlCl_3$ on Specific Conductivity of L-62, P-104 and Brij-78 solutions 111

Appendix XIII: Effect of SDS on Specific Conductivity of L-62, P-104 and Brij-78 solutions 111

Appendix XIV: Effect of CTAB on Specific Conductivity of L-62, P-104 and Brij-78 solutions 112

Appendix XV: Effect of TX-114 on Specific Conductivity of L-62, P-104 and Brij-78 solutions 112

Appendix XVI: Effect of NaCl on Relative Viscosity of L-62, P-104 and Brij-78 solutions 113

Appendix XVII: Effect of Na_2SO_4 on Relative Viscosity of L-62, P-104 and Brij-78 solutions 113

Appendix XVIII: Effect of $AlCl_3$ on Relative Viscosity of L-62, P-104 and Brij-78 solutions 114

Appendix XIX: Effect of SDS on Relative Viscosity of L-62, P-104 and Brij-78 solutions 114

Appendix XX: Effect of CTAB on Relative Viscosity of L-62, P-104 and Brij-78 solutions 115

Appendix XXI: Effect of TX-114 on Relative Viscosity of L-62, P-104 and Brij-78 solutions 115

LIST OF FIGURES

Figure 2.1: Structures of cubic and hexagonal crystalline phases 15
Figure 2.2: Isothermal phase diagram of $EO_{19}PO_{43}EO_{19}$-water- *p*-xylene ternary system at 25 ^{0}C 24
Figure 2.3: Phase diagram of Pluronic L64-water-*p*-xylene ternary system at 25^{0}C29
Figue 2.4: Phase diagrams of $EO_{20}PO_{70}EO_{20}/D_2O$/n-butyl acetate $EO_{20}PO_{70}EO_{20}/D_2O$/ butan-1-ol $EO_{100}PO_{70}EO_{100}/D_2O$/n-butyl and $EO_{100}PO_{70}EO_{100}/D_2O$/ butan-1-ol.. 31
Figure 2.5: Gibbs Isothermal phase diagram of P104-water- p-xylene ternary system at 25 ^{0}C.. 34
Figure 3.1: Gibbs Triangle for isothermal ternary phase diagram construction 48
Figure 4.1: Isothermal phase diagram of the P104/D_2O/benzyl alcohol ternary system at 25 ^{0}C.. 55
Figure 4.2: A SAXS diffraction pattern of samples in the l_1 region for the P104/D_2O/benzyl alcohol system at 25^{0}C... 57
Figure 4.3: A SAXS diffraction pattern of samples in the H_1 region for the P104/D_2O/Benzyl Alcohol system at 25^{0}C.. 58
Figure 4.4: A SAXS diffraction pattern of samples in the Lα region for P104/D_2O/benzyl alcohol system at 25^{0}C 59
Figure 4.5: Isothermal phase diagram of the L62/D_2O/Benzyl alcohol ternary system at 25 ^{0}C.. 61
Figure 4.6: A SAXS diffraction pattern of samples in the Lα the region for the P104/D2O/benzyl alcohol system at 25 ^{0}C... 63
Figure 4.7: Cloud point versus concentration of L-62... 67
Figure 4.8: Cloud Point versus concentration of P-104... 67
Figure 4.9: Effect of NaCl concentrations on Cloud Point of L-62, P104 and Brij-78 (1 wt% polymer).. 69
Figure 4.10: Effect of Na_2SO_4 concentration on Cloud Point of L62, P104 and Brij-78 (1 wt% polymer)... 69
Figure 4.11: Effect of $AlCl_3$ concentration on Cloud Point of L62, P104 and Brij-78 (1 wt% polymer).. 70
Figure 4.12: Cloud Point L62 (1 wt%) versus wt% of TX-114 73
Figure 4.13: Cloud Point of P104 (1 wt%) versus wt% of TX-114 73
Figure 4.14: Specific Conductivity of aqueous solution of L62 versus concentration. 75
Figure 4.15: Specific Conductivity of aqueous solution of P104 versus concentration 75
Figure 4.16: Specific Conductivity of aqueous solution of Brij-78 versus concentration 76
Figure 4.17: Specific Conductivity of NaCl in 1 wt% of L62, P104 and Brij-78.... 77
Figure 4.18: Specific Conductivity of Na_2SO_4 in 1 wt% of L62, P104 and Brij-78 78
Figure 4.19: Specific Conductivity of $AlCl_3$ in 1 wt% of L62, P104 and Brij-78 ... 78
Figure 4.20: Effect of SDS on Specific Conductivity of solutions of L62, P104 and Brij-78 81

Figure 4.21: Effect of CTAB on Specific Conductivity of solutions of L62, P104 and Brij-78 81
Figure 4.22: Effect of increasing wt% of TX-114 on Specific Conductivity of L62, P104 and Brij-78 solutions at a decreasing wt% of each polymer 83
Figure 4.23: Relative viscosity as a function of L62 concentration 85
Figure 4.24: Relative viscosity as a function of P104 concentration 85
Figure 4.25: Relative viscosities as a function of Brij-78 concentration 86
Figure 4.26: Relative Viscosity of a 1 wt% of L62, P104 and Brij-78 solution as a function of NaCl concentration 87
Figure 4.27: Relative Viscosity of a 1 wt% of L62, P104 and Brij-78 solution as a function of
Na_2SO_4 concentration 88
Figure 4.28: Relative Viscosity of a 1 wt% of L62, P104 and Brij-78 solution as a function of $AlCl_3$ concentration 88
Figure 4.29: Relative Viscosity of a 1 wt% L62, P104 and Brij-78 solutions versus SDS surfactant concentration 90
Figure 4.30: Relative Viscosity of a 1 wt% L62, P104 and Brij-78 solutions versus CTAB surfactant concentration 90
Figure 4.31: Effect of increasing wt% of TX-114 on relative viscosity of L62 at a decreasing wt% of polymer 92
Figure 4.32: Effect of increasing wt% of TX-114 on relative viscosity of P104 at a decreasing wt% of polymer 92
Figure 4.33: Effect of increasing wt% of TX-114 on relative viscosity of Brij-78 at a decreasing wt% of polymer 93

LIST OF ABBREVIATIONS

Brij-78	Polyoxyethylene (20) Stearly Ether
CMC	Critical Micelle Concentration
Conc.	Concentration
CP	Cloud Point
CTAB	Cetyl Trimethyl Ammonium Bromide
HLB	Hydrophilic-Lipophilic Balance
O/W	Oil to Water
W/O	Water to Oil
SDS	Sodium Dodecyl Sulphate
TX- 144	Triton 114
PEO or EO	Polyethylene Oxide
PPO or PO	Polypropylene Oxide
SAXS	Small Angle X-ray Scattering
L62	Poly(ethylene oxide)$_6$-Poly(propylene oxide)$_{34}$-Poly(thylene oxide)$_6$
P104	Poly(ethylene oxide)$_{27}$-Poly(propylene oxide)$_{61}$-Poly(thylene oxide)$_{27}$
PEO-PPO-PEO	Poly(ethylene oxide)-Poly(propylene oxide)-Poly(thylene oxide) Block Copolymer
w/v	Weight to volume
Lα	Lamellar Phase
H_1	Normal Hexagonal Phase
H_2	Reverse Hexagonal Phase
L_1	Normal Micellar Solution
L_2	Reverse Micellar Solution
I_1	Normal Micellar Cubic Phase
I_2	Reverse Micellar Cubic Phase
V_1	Normal Biscontinuous Cubic Phase
V_2	Reverse Bicontinuous Cubic Phase
CMT	Critical Micelle Temperature
CPT	Cloud Point Temperature

ACKNOWLEDGEMENT

My special thanks go to the Almighty Father in Heaven for the strength, courage and patience that He gave me that enabled me to undertake the study and complete it.

I wish to most sincerely thank my research supervisors: Prof. P. Kipkemboi and Dr. M. O. Okoth for their pieces of advice, encouragement and corrections they made to this work which enabled me come this far. Next, I thank the entire Department of Chemistry technical staff of University of Eldoret for their support while carrying out the experimental work of the study from Chemistry Laboratory. My other thanks go to University of Eldoret Botany Department technical staff for allowing me the opportunity to use their laboratory and centrifuging machine. I wish also to thank most sincerely Katarina Flodström of the Department of Physical Chemistry 1, counter for Chemistry and Engineering, Lund University, Sweden for conducting a SAXS measurement on the samples.

I also thank my friends who include C. Otara, Osoro, Osano, Olal, Marende, and A. Nyakweba for their moral support and positive criticism that made me to make appropriate adjustment to the study.

Finally, I thank my entire family members consisting of my wife Christine and children Marion, Michelle, Sandra and Mogonchi jnr., my parents Mr. and Mrs. I. Mogonchi; brothers Japhet, Douglas, Wyckliffe and Geoffrey and Sisters Tabitha, Everline and Hilder for their timely encouragement support and prayers that saw me complete this work.

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

In the last decades, an important insight has triggered a tremendous upsurge of interest on surfactant structures. This was in recognition of the fact that these structures can mimic biological structures in some ways (Fendler, 1982). They are among the most versatile chemicals available to chemists, used in a variety of areas including production and processing of different foods, in agrochemical industry, in pharmaceutical industry, in personal care and laundry products, in petroleum industry, in polymerization processes, in mining of mineral ores, in fuel additives and lubricants, in paints, adhesives and photographic films. They can also be found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental, health, and safety applications (Satan and Sawant, 2006).

Interest of nonionic surfactants of oxy-ethylene group and the self-assembly of PEO-PPO-PEO block copolymers has grown considerably over the last decade. Tri-block copolymers with composition PEO-PPO-PEO where PEO and PPO are poly(ethylene oxide) and poly(propylene oxide) respectively are a group of non-ionic surfactants (commercially available as Pluronics, Synperonics or Poloxamers), which displays amphiphilic behavior. Tailoring the copolymer composition and molecular weight in the manufacturing process results in a wide range of products with optimum properties suitable for use in a variety of industrial areas. As a result, PEO–

PPO–PEO copolymers have found widespread industrial applications in such areas as detergency, foaming/defoaming, emulsification, dispersion stabilization, lubrication, as well as some more special application fields as cosmetics, pharmaceuticals, and bioprocessing (Alexandridis *et al*., 1995; Chu, 1995).

Solution properties of the PEO-PPO-PEO copolymers depend strongly on the interaction of polymer segments with the solvent. The PPO middle block is more hydrophobic than the PEO end ones. Both types of blocks become more hydrophobic at high temperatures and at 25 ^{0}C and higher, the PPO is for all practical purposes hydrophobic (Svensson *et al.*, 1999a). Therefore, in aqueous solutions, the PEO-PPO-PEO block copolymers self-associate into micellar like aggregates with a core dominated by PPO segments surrounded by water swollen PEO blocks. At a fixed temperature, the concentration at which the first micelles start to form is referred to as critical micelle concentration (CMC) (Chu and Zhou, 1996). Another way to induce self-assembly of PEO-PPO-PEO block copolymers is to increase the temperature. The temperature at which micelle begin to form now at a fixed concentration is called critical micelle temperature (CMT) (Alexandridis *et al*, 1994).

Formation of micelles and their shape and size have been investigated by a number of researchers using various techniques and are now relatively known. Some of the PEO-PPO-PEO copolymers have been found to form gels in water and some of the gel phases reported in literature correspond to a cubic organization while others still lack proper structural identification. Although the PEO-PPO-PEO copolymers are good emulsifiers and can solubilize hydrophobic compounds in aqueous micellar solutions, phase behavior of ternary copolymer-water-oil systems have not been very widely studied (Hurter *et al.*, 1995). Most studies that have been reported are those that have used p-xylene as the non-polar solvent (Alexandridis *et al.*, 1995; Svensson *et al.*, 1999b; Svensson *et al.*, 1998; Zhou *et al.*, 1996).

Over the recent past years, new surfactant molecules have been appearing at a relatively rapid pace and there is an emphasis on increasing the understanding of basic performance of surfactant formulations and the provision of new surfactant technologies to a diverse range of disciplines.

In this study, three nonionic surfactants were used, which were; L-62 $\{(EO)_6(PO)_{34}(EO)_6\}$, P104 $\{(EO)_{27}(PO)_{61}(EO)_{27}\}$ and Brij-78 [polyoxyethylene (20) stearyl ether $[C_{18}H_{37}(OCH_2CH_2)_nOH)]$. Pluronic P104 is a block copolymer with the highest molecular weight (5900g/mol). Phase behaviors of ternary systems: L-62/D_2O/benzyl alcohol and P104/D_2O/benzyl alcohol were determined and the phases obtained used to draw isothermal phase diagrams for each system. Cloud Points (CP), Specific Conductivities (SC) and Relative Viscosities (RV) of solutions of the three nonionic surfactants were determined at different surfactant concentrations. This procedure was conducted on mixtures of the surfactants with other surfactant additives; Triton X-114, sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB). The effect of inorganic salt additives on CP, SC and RV of the three surfactants were also studied using sodium chloride, sodium sulphate and aluminium chloride as the inorganic salts.

1.2 Statement of the Problem

Most studies on phase behavior of ternary systems “polymer/water/oil” have addressed effect of molecular weight and composition of polymer on phase behavior (Alexandridis *et al.*, 1995; Alexandridis *et al.*, 1998; Svensson *et al.*, 1998; Zhou *et al.*, 1996; Kipkemboi *et al.*, 2003; Svensson *et al.*, 1999b) and all have used *p*-xylene as the non-polar solvent. Therefore, little has been done on the effect of solvent (oil) quality, especially by use of different oils, on phase behavior, structure and aggregation of such surfactant systems.

In this study benzyl alcohol was used in place of the most commonly used *p*-xylene with the aim of determining whether it enhances the formation of a bigger number of mesophases and different aggregation behavior of the two copolymer/D_2O/oil ternary systems. This would help in providing an understanding of phase behavior, structure and aggregation of triblock (copolymer/water/oil) systems of non-ionic surfactants when other oils are used. In this study, the effect of solvent quality on phase behavior of ternary systems: P104/water/benzyl alcohol and L-62/water/benzyl alcohol were addressed.

Due to the introduction of new products into the market, detailed studies on the physico-chemical properties need to be done for good understanding of their applications. The study addressed cloud point (CP) formation, specific conductivity (SC), and relative viscosity (RV) of pluronic P-104, pluronic L-62 and Brij- 78 non-ionic surfactants when in pure solutions or with inorganic salt and other surfactant additives. This was done for better understanding of the important properties of these surfactants which will then guide on their applications.

1.3 Study Objectives

1.3.1 Major Research Objective

To determine the phase behavior and aggregation of tri-block copolymers L-62, P104 in water and benzyl alcohol ternary systems and physico-chemical properties of L62, P104 and Brij-78 non-ionic surfactant solutions

1.3.2 Specific Research Objectives

i. To establish the different phases formed by L-62/water/benzyl alcohol and P104/water/benzyl alcohol ternary systems

ii. To determine isothermal ternary phase diagrams of L-62/water/benzyl alcohol and P104/water/benzyl alcohol systems

iii. To determine the cloud points (CP), specific conductivities (SC) and relative viscosities (RV) of aqueous solutions of L-62, P104 and Brij-78

iv. To determine the effect of inorganic salt additives on CP, SC and RV of aqueous solutions of L-62, P104 and Brij-78

1.4 Justification of the Study

Nonionic surfactants are generally inexpensive and have many potential applications such as cosmetics, detergency, pharmaceuticals, ore floatation and cloud point extraction methods, drilling fluids, and enhanced oil recovery processes (Rosen, 1989). Amphiphilic block copolymers can form self-assembled aggregates when dissolved in a selective solvent which increases their uses (Tuzar and Kratochvil, 1993). Understanding and control of self-assembly depends on how the nature of oil present affects phase behavior and structure afforded by amphiphilic block copolymers. Oil can swell to varying degree the hydrophobic part of amphiphile and thus its selection is of great importance in modulating the interfacial curvature.

The role played by solvent in micelle formation is largely responsible for self-organization on amphiphilic molecules into micelles and liquid crystals (Callaghan *et al*., 1993). From the literature studied, benzyl alcohol and other non-polar solvents have rarely been used and hence the need to study the behavior of some of these surfactants with it as a selective solvent for hydrophobic parts of the nonionic surfactants.

Physico-chemical investigations of surfactants in aqueous solutions with or without cosolvents are important in understanding the nature and mechanism of intermolecular interactions in these systems. Studies of physico-chemical properties of aqueous solutions of surfactants, their relevance in biological systems and their intriguing and fascinating features continuously provide new challenges to the scientific community. These properties are of significant importance especially on issues to do with enhanced oil recovery, detergency and concentration of ores by froth floatation in metallurgical processes (Sansanwal, 2006).

Physico-chemical properties of an aqueous solution of mixed surfactants change with increase in surfactant concentration according to the way aggregates form. A mixture of surfactants forming insoluble aggregates and mixed micelles has become very important in industrial applications and surface chemical work of surfactants because of the tendency to form aggregated structures which are very different from those formed by solutions with pure surfactants. Some phenomena, which are not expected to occur in pure solution systems, do occur in aqueous solutions containing mixtures of surfactants (Satan and Sawant, 2006).

CHAPTER TWO

LITERATURE REVIEW

2.1 General Information about the Study

Some compounds, such as short-chain fatty acids, are amphiphilic or amphiphatic in nature. These compounds form oriented monolayers at interfaces and show surface activity. These compounds are called surface active or surfactants. In some usage surfactants are defined as molecules capable of associating to form micelles. These compounds are termed surfactants,

amphiphiles, surface-active agents, tensides, or, in the very old literature, paraffin-chain salts. They lower surface tension of water or interfacial tension between two liquids or between a liquid and a solid. They concentrate at the surface and solubilize materials with little natural affinity to one another (Laurier *et al*., 2003).

Surface-active compounds possess characteristics that are valuable such as emulsification, wetting, water-proofing and spreading which make them to find application in detergents, food industries, pharmaceutical industries, enhanced oil recovery, metallurgical processes for concentrating ores, solubilization of water insoluble dyes, hydrocarbons, analytical chemistry and in biological and environmental systems (Sinha *et al*., 2002).

Surfactants display a number of distinct solution properties in water which can be ascribed to the presence of hydrophilic head group and hydrophobic chain (tail) in the molecule. The polar head group usually interacts strongly with its aqueous environment and is solvated via dipole-dipole or ion-dipole interactions. For the non-polar chains, interaction with water takes place only weakly, resulting in the formation of ordered water molecules near the non-polar chain (Boucher *et al*., 1998). Characteristic features of surfactants include: amphiphatic structure, solubility, adsorption at interfaces, and orientation at the interfaces, micelle formation, critical micelle concentration and functional properties. They are among the most versatile chemicals available to chemists, used in a variety of areas including chemical kinetics and as membrane mimics in biochemistry. The application of surfactant technology to a number of industrial and pharmaceutical processes has been intensely investigated (Karsa, 1987).

2.2 Classifications of Surfactants

Surfactants are classified depending on the charge of the surface active moiety, usually the larger part of the molecule. These classes are: anionic, cationic, nonionic and zwitterionic. Anionic surfactants carry a negative charge as in soap. Carboxylate, sulfate, sulfonate and phosphate are the polar groups found in anionic surfactants, cationic surfactants carry a positive charge and the functional parent structure is of the type $(C_{18}H_{37})_2N^+(CH_3)_2Cl^-$, nonionic surfactants have no charge on their molecules and the solubilizing combination is supplied by a chain of ethylene oxide groups as in $C_{15}H_{31}((OC_2H_2)_7OH_2)$ while zwitterionic surfactants have both positive and negative charges which provide the solubilization of the molecule as in the molecule $C_{12}H_{25}N^+((CH_3)_2CH_2CO_2^-)$ (Hunter, 1987)

2.2.1 Nonionic Surfactants

Nonionic surfactants represent a class of surfactants, which as the name suggests, have no charge and therefore carry no discrete charges when dissolved in water or in aqueous solutions. This class of surfactants is inexpensive and has many potential applications such as cosmetics, detergency, pharmaceuticals, ore floatation and cloud point extraction methods, drilling fluids, and enhanced oil recovery processes**.** A major reason for the wide range of uses of this class of surfactants is that it is possible to control the hydrophilic-lipophilic balance (HLB) and hence the interfacial properties of surfactant/oil systems (Furlong and Aston, 1982).

Nonionic surfactants have amphiphilic molecules with nonionic hydrophilic group. Theoretically, their properties, especially the solubility, must be easier to investigate than for ionic surfactants, because of the lack of long-range electrostatic interactions. These type of surfactants owe their solubility in water to the hydration of polyethylene oxide chains, therefore, solubility increases as the chain length increases (Travalloni-louvisse and Gonzalez, 1988)

2.3 Polymorphism in Surfactants

All the studies made by now on usual surfactants, have revealed that the phases appearance process and their succession in diagrams, are qualitatively similar for all surfactants and are not related to the chemical structure of both the polar head and the hydrocarbon chain, thus demonstrating the validity of the packing parameter theory (Gabriela, 2004).

The surfactant solubility increase is generated by the monomers aggregation process that starts at critical micelle concentration (CMC) and improves by means of the hydrophobic effect until the apparition of the ordered structures. Ionic surfactants, solubility is rather low because of the high stability of their crystals; so, an efficient way to increase solubility requires chemical changes of the amphiphilic molecules in order to modify their packing into the crystal (Gabriela, 2004).

Block copolymers and surfactant systems are similar to each other, in that, they both exhibit very rich polymorphism. Block copolymer systems, however, have greater advantages over surfactant systems with respect to modification of the systems using techniques such as bending, nonlinear architecture and multiblock copolymers. As the system becomes more complex, the phase behavior is also expected to become more complex, thus, there will be a greater chance of finding a new morphology (Hirokazu, H., 1998).

2.4 Ternary Solution Systems

When adding an adequate third component to the binary lyotropic solutions, the phase diagrams are essentially modified. The third components usually are electrolytes, oils or cosurfactants.

When oils are added, they are solubilized either inside the micelles, increasing their radius and giving rise to cubic (I_1) and hexagonal (H_1) phases, or at the micelles surface, reducing micelle curvature and giving rise to the lamellar (Lα) phase. All phases may appear in both normal and reversed structures (Gabriela, 2004).

Cosurfactants are substances such as alcohols, fatty acids and long chain aldehydes**,** and are insufficiently hydrophilic to form micelles in aqueous solutions. An insoluble substance in a certain solvent can be “solubilized” when adding an amphiphilic component to the solution that becomes an isotropic ternary solution, which is thermodynamically stable. This process can happen only in the presence of normal micelles in aqueous solutions and of reversed micelles in nonpolar solutions. Only micellar solutions remain fluid and isotropic in the presence of the solubilized substances. The liquid crystal phases are anisotropic and conserve a relatively high viscosity. Hence, the presence of the association micelles is determinant for the solubilization process; if the insoluble substance is amphiphilic too, then mixed micelles form and a lyotropic ternary solution results. If association micelles are of a nonionic surfactant aqueous solution, then there is a supplementary possibility to solubilized cosurfactants in the ethylene oxide (EO) zone of the amphiphilic molecules (Gabriela, 2004).

2.5 Liquid Crystals

Liquid crystals are a distinct phase of condensed matter which typically form under conditions that lie between those of solids and melts. Certain organic materials, on heating, do not just show a single transition from crystal to liquid but rather, a series of transitions involving intermediate phases. The mechanical, optical and symmetry properties of these phases are intermediate between those of liquids and crystals. A liquid crystal is an intermediate phase which has a liquid-like order in at least one direction and possesses a degree of anisotropy which is a characteristic order. Therefore, the intermediate phases are called liquid crystalline (LC) phases (or mesophases). Liquid crystalline phases are exhibited by different several systems. In addition to certain types of organic systems, micellar solution of surfactants, main and side chain polymers and a large number of biological systems are known to have liquid crystalline properties (De Gennes, 2001). Many common fluids, such as soapy water, are in fact liquid crystals. Soap forms a variety of LC phases depending on its concentration in water (Luzzati *et al.*, 1957).

The ordering of liquid crystalline phases is extensive on the molecular scale. This order extends up to the entire domain size, which may be on the order of micrometers, but usually does not extend to the macroscopic scale as often occurs in classical crystalline solids. However some techniques, such as the use of boundaries or an applied electric field, can be used to enforce a single ordered domain in a macroscopic liquid crystal sample. The ordering in a liquid crystal might extend along only one dimension, with the material being essentially disordered in the other two directions (Collings and Hird, 1997).

2.5.1 Thermotropic Liquid Crystals

Thermotropic liquid crystals exhibit a phase transition into the LC phase as temperature is changed. These LCs consist of organic molecules and they are those that occur in a certain temperature range. In thermotropic liquid crystals, phase transitions are brought about by changing temperature of the system (Collings and Hird, 1997). If the temperature rise is too high, thermal motion will destroy the delicate cooperative ordering of the LC phase, pushing the material into a conventional isotropic liquid phase. At too low temperature, most LC materials will form a conventional crystal. Many thermotropic LCs exhibit a variety of phases as temperature is changed. For instance, a particular type of LC molecule (called mesogen) may exhibit various smectic and nematic (and finally isotropic) phases as temperature is increased. An example of a compound displaying thermotropic LC behavior is para-azoxyanisole (Madsen *et al.*, 2004).

2.5.2 Lyotropic Liquid Crystals

A lyotropic liquid crystal exhibits liquid-crystal behavior when it reacts with water or a specific solvent (Matsumoto and Kadota, 1991). Lyotropic liquid crystals consist of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. These LCs exhibit phase transitions as a function of both temperature and concentration of the LC molecules in a solvent (typically water). Many amphiphilic molecules show lyotropic liquid-crystalline phase sequences depending on the volume balances between the hydrophilic part and hydrophobic part. These structures are formed through the micro-phase segregation of two incompatible components on a nanometer scale. In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system (Qizhen *et al.*, 2005).

In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases. This class of crystals comprises multi-component systems and they show a rich variety of phases (Gilbart *et al.*, 1994).

The content of water or other solvent molecules changes the self-assembled structures. At very low amphiphile concentration, the molecules will be dispersed randomly without any ordering. At slightly higher (but still low) concentration, amphiphilic molecules will spontaneously assemble into micelles or vesicles. This is done so as to 'hide' the hydrophobic tail of the amphiphile inside the micelle core, exposing a hydrophilic (water-soluble) surface to aqueous solution but these spherical objects do not order themselves in solution. At higher concentration, the assemblies will become ordered. A typical phase is a hexagonal columnar phase, where the amphiphiles form long cylinders (again with a hydrophilic surface) that arrange themselves into a roughly hexagonal lattice. This is called the middle soap phase. At still higher concentration, a lamellar phase (neat soap phase) may form, where extended sheets of amphiphiles are separated by thin layers of water. For some systems, a cubic (also called viscous isotropic) phase may exist between the hexagonal and lamellar phases, where spheres are formed that create a dense cubic lattice. These spheres may also be connected to one another, forming a bicontinuous cubic phase.

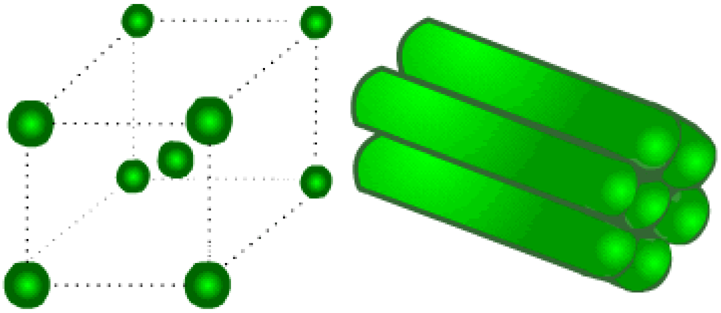
The objects created by amphiphiles are usually spherical (as in the case of micelles), but may also be disc-like (bicelles), rod-like, or biaxial (all three micelle axes are distinct). For some systems, at high concentrations, inverse phases are observed. That is, one may generate an inverse hexagonal columnar phase (columns of water encapsulated by amphiphiles) or an inverse micellar phase (a bulk liquid crystal sample with spherical water cavities).

Many biological structures such as the brain, nerve system, muscle, and blood contain lyotropic liquid crystals. The lyotropic liquid crystals are primarily investigated in the fields of biochemistry, biophysics, and bionics. These crystalline phases are exhibited by amphiphilic molecules when they are dissolved above a certain concentration in a solvent which is usually water. Liquid crystal phase transitions are brought about by changing relative concentration of various components or sometimes temperature. This class of liquid crystals is extremely important because of their role in biological membranes. Membranes are composed of amphiphilic lipids mostly phospholipids and chorestrol with a small percentage of glycolipids (Gilbart *et al.*, 1994).

2.5.3 Classification and Uses of Lyotropic Liquid Crystals

Lyotropic liquid crystal (LLC) systems that commonly consist of amphiphilic molecules and solvents can be classified into a number of phases such as lamellar ($L\alpha$), normal hexagonal (H_1), reverse hexagonal (H_2), normal bicontinous cubic (V_1), reverse bicontinous cubic (V_2), normal micellar cubic (I_1), reverse micallar cubic (I_2) mesophases, and so on. In recent years, LLC systems have received considerable attention because of their excellent potential as drug vehicles. Among these systems, reversed cubic (I_2) and reversed hexagonal (H_2) mesophases are the most important and have been extensively investigated for their ability to sustain the release of a wide range of bioactives from low molecular weight drugs to proteins, peptides and nucleic acids (Clogston and Caffrey, 2005).

The structures of micellar cubic crystal and hexagonal crystal are presented in Figure 2.1



Cubic crystalline structure Hexagonal crystalline structure

Figure 2.1 structures of cubic and hexagonal crystalline phases (*http//www.google*. (18.11.2013)

Reversed cubic and reversed hexagonal mesophases are formed by polar lipids in an aqueous environment. The structure-forming lipids can absorb a certain amount of water after which they spontaneously form gel-like phases with unique internal structures, into which drugs can be incorporated. These mesophases also have other important properties such as they are non-toxic, biodegradable and bioadhesive which contribute to their applications for drug delivery (Shah, 2001). Due to the infinite swelling capability, reversed cubic and hexagonal mesophases can also be dispersed in equilibrium with excess water and form colloidal dispersions with superior thermodynamic stability. Currently, reversed cubic and reversed hexagonal mesophases are being investigated to be used for aural, buccal, gastrointestinal, intravenous, lung, nasal, oral, rectal and vaginal administration of drug with considerable progress (Yaghmur and Glatter, 2009). Lyotropic liquid crystals also find useful applications in soap industries besides their use in medical field where they can be used to coat drugs to prevent them from being destroyed in the digestive tract. These drugs are taken orally and on reaching the proper location in the body, they are released by breaking down the liquid crystalline coating (Gilbart *et al.*, 1994).

2.5.4 Uses of thermotropic Liquid Crystals

Liquid crystals find wide applications in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field. In a typical device, a liquid crystal layer (typically 10 μm thick) sits between two polarizers that are crossed (oriented at 90° to one another). The liquid crystal alignment is chosen so that its relaxed phase is a twisted one and the device thus appears transparent. When an electric field is applied to the LC layer, the long molecular axes tend to align parallel to the electric field thus gradually untwisting in the center of the liquid crystal layer. In this state, the LC molecules do not reorient light, so the light polarized at the first polarizer is absorbed at the second polarizer, and the device loses transparency with increasing voltage. In this way, the electric field can be used to make a pixel switch between transparent or opaque on command. Color LCD systems uses the same technique, with color filters used to generate red, green, and blue pixels (Castellano, 2005).

Thermotropic chiral LCs whose pitch varies strongly with temperature can be used as crude liquid crystal themometers, since color of the material will change as the pitch is changed. Liquid crystal color transitions are used on many aquarium and pool thermometers as well as on thermometers for infants or baths. Other liquid crystal materials change color when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on. Liquid crystal in fluid form is used to detect electrically generated hot spots for failure analysis in semiconductor industry (Kopp *et al.*, 1998).

Liquid crystal lasers use a liquid crystal in the lasing medium as a distributed feedback mechanism instead of external mirrors. Emission at a photonic band-gap created by the periodic dielectric structure of the liquid crystal gives a low-threshold high-output device with stable monochromatic emission (Dolgaleva *et al.*, 2008).

2.6 Block Copolymers

The polymer blocks poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) can be combined to give PEO-PPO diblock copolymer and PEO-PPO-PEO triblock copolymer respectively where PEO is hydrophilic and PPO has hydrophobic ends. Water soluble triblock copolymers of the type PEO-PPO-PEO or $(EO)_a(PO)_b(EO)_c$, where a, b, c are the number of repeated units in the copolymer, are nonionic macromolecular surfactants with commercial names, poloxamers (ICI) or pluronics polyols (BASF) and in their many applications, the material may have two or more functions (Benjamin, 1995).

These block copolymers form a class of amphiphiles, developed originally for use as surface active agents in aqueous solutions, but shown to also form structures in the absence of any solvent**.** By tailoring the copolymer composition and molecular weight in the manufacturing process, a wide range of products with optimum properties suitable for use in a variety of industrial areas are produced. As a result, PEO–PPO–PEO copolymers have found widespread industrial applications in areas such as detergency, foaming/defoaming, emulsification, dispersion stabilization, lubrication, as well as some more special application fields as cosmetics, pharmaceuticals, and bioprocessing (Chu, 1995).

Block copolymers are known to associate into micelles when dissolved in a selective solvent, since they can also express amphiphilic character (Tuzar and Kratochvil, 1993).

2.7 Surfactant/water/oil Self-assembly

Surfactants and lipids in solution can form thermodynamically stable supramolecular assemblies such as micelles in aqueous solutions, microemulsions in multi component systems with water, oil, and, often, cosurfactant and lyotropic liquid crystals (lamellar, hexagonal and cubic) as well as kinetically stabilized vesicles (Lacic, 1993).

Block copolymers consisting of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are an interesting class of amphiphiles, which were originally developed for use as surface active agents in aqueous solutions but shown to also form structures in the absence of any solvent. A number of PEO-PPO-PEO block copolymers can self-associate in water, at concentrations that depend on temperature, in the form of micelles that have a core composed of PPO and a corona dominated by PEO segments. The formation of micelles and their shape and size have been investigated using various techniques and are relatively understood. A notable feature that distinguishes the self-assembling behavior of PEO-PPO-PEO block copolymers from that of low-molecular-weight surfactants is the ability to exhibit much richer structural polymorphism and to form a great variety of both normal and reverse liquid crystalline microstructures (Svensson *et al.*, 1999b).

Investigations indicate that PEO/PPO block copolymers can self-assemble in water into lyotropic liquid crystals (having lamellar, hexagonal, or cubic structures, with one-, two-, or three-dimensional order, respectively), the same applies to common surfactants. A number of PEO-PPO-PEO triblock copolymers have been identified which self-assemble under equilibrium conditions into a variety of lyotropic liquid crystalline microstructures consisting of spherical, cylindrical, or planar microdomains, of normal (“oil”-in-“water”) or reverse (“water”-in-“oil”) morphology and discrete or interconnected (bicontinuous) topology (Alexandridis *et al.*, 1995).

The variety of structures formed by a PEO/PPO block copolymer in the presence of solvents is much greater than that of a block copolymer of a given block composition in the absence of solvents or even in the presence of homopolymers. For a PEO/PPO block copolymer of a given block composition and molecular weight, the types of structures obtained in the presence of selective solvents appear to be a function of the volume fraction of the polar ("water"-like)/apolar ("oil"-like) components; this has been attributed to the ability of the macromolecular blocks to swell to a different extent with respective solvents and to thus modulate the interfacial "curvature" and resulting structure (Alexandridis *et al.*, 1998).

2.8 Ternary Block Copolymer-water-oil Systems

Ternary systems are those that have three components, for example, block copolymer/water/oil systems.

2.8.1 Phase behavior of block copolymer/water/oil ternary systems

Over the last years, the phase behavior and microstructure of a number of PEO-PPO-PEO block copolymers have been examined in the presence of water and xylene as selective solvents for the PEO and PPO blocks respectively (Alexandridis *et al.*, 1995; Zhou *et al.*, 1996; Svensson *et al.*, 1998; Kipkemboi *et al.*, 2003).

Alexandridis and coworkers (1998) investigated on $(EO)_{19}(PO)_{43}(EO)_{19}$-$2H_2O$-*p*-xylene ternary system that gave a record nine different phases. This ternary system produced the highest number of phases and as a result, the block copolymer pluronic

P84 ($EO_{19}PO_{43}EO_{19}$) has been used to discuss the phase behavior and microstructure systems. This ternary system gave a record nine phases as shown in Figure 2.2.

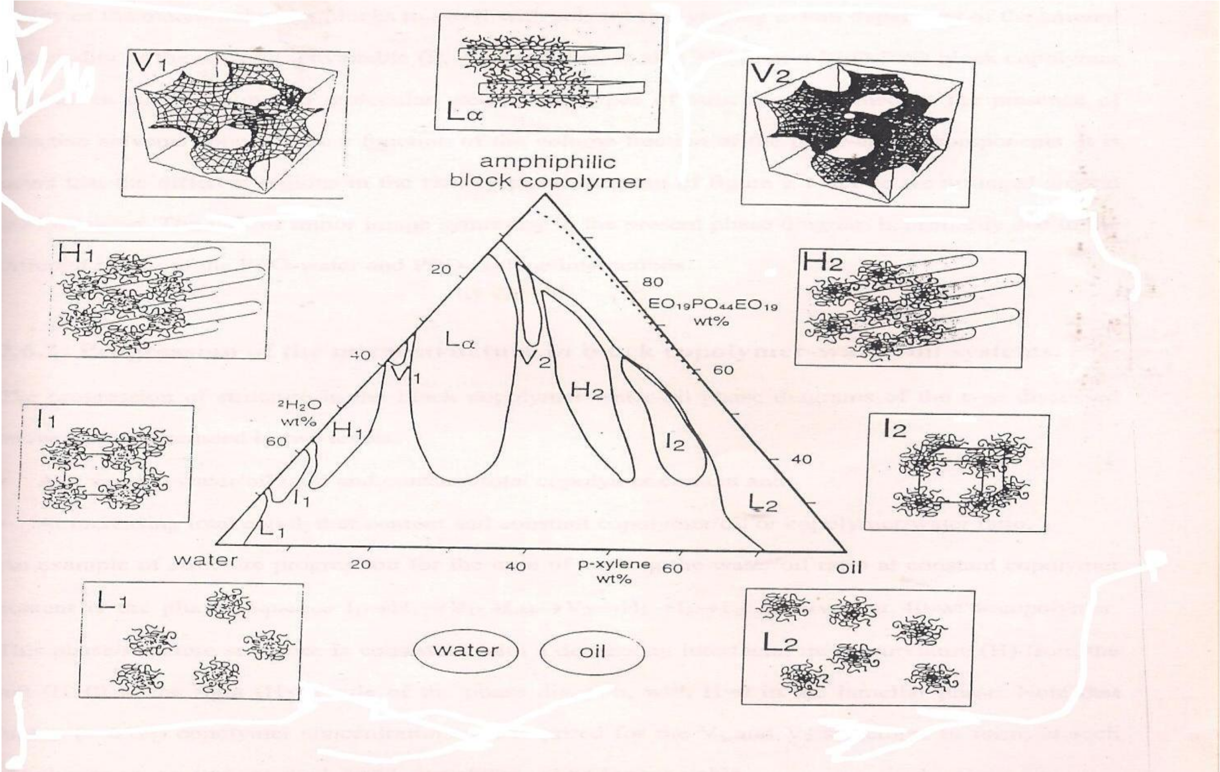


Figure 2.2 Isothermal phase diagram of $EO_{19}PO_{43}EO_{19}$-water- *p*-xylene ternary system at 25 ^{0}C. (Alexandridis *et al.*, 1998).

These phases consist of seven different lyotropic liquid crystalline phases which are: lamellar phase (L_{α}), normal hexagonal (H_1), reverse hexagonal (H_2), normal bicontinous cubic (V_1), reverse bicontinous cubic (V_2), one with high oil/water ratio; normal micellar cubic (I_1), and one with high water/oil ratio; reverse micallar cubic (I_2) and L_1 and L_2 which denote water-rich (normal micellar) and water-lean/oil-rich (reverse micellar) solutions. So far this ternary system is the one that has produced the highest number of phases. Phases such as cubic, hexagonal and/or lamellar mesophases can be formed at higher copolymer concentrations that are higher than 20% (Alexandridis *et al.*, 1998).

2.8.2 Characterization of Lyotropic Liquid Crystals

In characterization of lyotropic liquid crystalline phases, there is a strong emphasis on the use of diffraction processes such as Small-Angle X-ray Scattering (SAXS) or Small-Angle Neutron Scattering (SANS). Most mesophases are conventionally distinguished on the basis of diffraction features (Stephen, 2001).

Lamellar (Lα) phase gives a typical signature of smectic lattice: equally spaced peaks corresponding to α, 2α, 3α, e.t.c where α is the spacing between adjacent bilayers. Entropically driven fluctuations of the bilayers can bend them until they lose their planar structure which may lead to punctures and channels between bilayers. Conventionally, a lamellar phase is optically anisotropic, and also exhibits a smectic diffraction pattern (Stephen, 2001).

Columnar mesophases: Hexagonal (H_1 and H_2) mesophases are of intermediate viscosity to discrete micellar and bicontinuous cubic phases. The standard picture of a hexagonal mesophase consists of a dense packing of cylindrical micelles arranged on a 2D hexagonal lattice. It is often identified by characteristic fan texture in the optical microscope due to focal conic domains of columns. In contrast to lamellar phase which is equally curved towards both sides, hexagonal phases are of two types; type 1 where s=1/2 and type 2 where s □1. In all cases, X-ray scattering has revealed that the chains are molten, and SAXS spectrum gives a number of Bragg peaks in the ratio 1:√3:√4: e.t.c (Stephen, 2001).

Globular Mesophases: Discrete Micellar (I_1 and I_2) are more freely flowing and less viscous than lamellar mesophases due to their discete globular micellar structure. These phases are optically isotropic and no texture is visible. The phases also occur in pairs: Type 1 has s= 1/3 and type 2 has s □1 (Stephen, 2001).

Bicontinuous mesophases exhibit the most complex spatial organization of all known lyotropic liquid crystals. They are very viscous and nearly solid in some cases. All cases exhibit cubic symmetries and therefore, they do not display optical features. These mesophases are structurally warped as lamellar phases but their major difference is that they contain a single bilayer membrane, or hyperbolic geometry. They also occur in two types: type 1, s=2/3 and type 2, s □1. The Bragg peaks occur at positions √2, √4, √6, e.t.c (Stephen, 2001).

Molten mesophases: isotropic solutions (L_1 and L_2) are characterized by poor spatial correlations. Small-angle scattering spectra typically exhibit a single broad scattering peak at small angles. These phases resemble liquids: they have local (meso) structure, but the very short-range ordering is insufficient to define a lattice, the aggregates in these mesophases are thus disordered (Stephen, 2001).

2.8.3 Isothermal Ternary Phase Diagrams

A novel development in the field of amphiphilic block copolymers is the discovery that ternary isothermal systems consisting of a PEO/PPO block copolymer, “water”, and “oil” (where “water” and “oil” are selective solvents for the PEO and PPO blocks, respectively) can exhibit a very rich structural polymorphism (Holmqvist *et al.*, 1997).

Isothermal ternary phase diagram of $(EO)_{19}(PO)_{43}(EO)_{19}$-$2H_2O$-*p*-xylene ternary system that gave a record nine different phases is shown in Figure 2.2. A record of nine regions of different microstructures is presented in this phase diagram. Seven different lyotropic liquid crystalline phases have been identified and characterized in terms of microstructures. These are: lamellar (L_α), normal hexagonal (H_1), reverse hexagonal (H_2), normal bicontinous cubic (V_1), reverse bicontinous cubic (V_2), one with high oil/water ratio; normal micellar cubic (I_1), and one with high water/oil ratio; reverse micallar cubic (I_2) with L_1 and L_2 which denote water-rich (normal micellar) and water-lean/oil-rich (reverse micellar) solutions (Alexandridis *et al.*, 1998).

The modulation of interfacial curvature can be attributed to the ability of macromolecular blocks to swell with solvent to a varying degree depending on amount and quality of the solvents. For a PEO-PPO-PEO block copolymer of a given composition and molecular weight, the types of structures obtained in the presence of selective solvent appear to be a function of the volume fraction of the polar/apolar components. It is noted that the different regions in the ternary phase diagram as presented in Figure 2.2 are arranged around the lamellar phase region. The lack of mirror/minor image symmetry in the present phase diagram is primarily due to the different nature of PEO/water and PPO/xylene interactions (Alexandridis *et al.*, 1998).

The copolymer examined here, $(EO)_{19}(PO)_{43}(EO)_{19}$ (Pluronic P84), has a 45% higher molecular weight than, but is of the same composition as $(EO)_{13}(PO)_{30}(EO)_{13}$ (Pluronic L64), which gives a smaller number of phases at same conditions. The ternary system of $(EO)_{13}(PO)_{30}(EO)_{13}$/water/xylene at 25 ^{0}C gave a total of seven phases; two isotropic solution phases, one rich in water (L_1) and another with a high p-xylene to water ratio (L_2) and four liquid crystalline phases lamellar ($L\alpha$), normal (H_1) and reverse hexagonal (H_2), reverse bicontinuous cubic (V_2) phase and in addition to these, a narrow isotropic phase was found between L_1 and H_1 regions (Alexandridis *et al.*, 1995). An increase in the composition stability range of the different structures and a formation of more types of lyotropic liquid crystalline structures is observed with P84, as compared to L64 (Alexandridis *et al.*, 1998).

The ternary system consisting of Pluronic P104 $(EO)_{27}(PO)_{61}(EO)_{27}$ in the presence of water and xylene at 25 ^{0}C gave eight phases which are lamellar ($L\alpha$), normal (H_1) and reverse hexagonal (H_2), reverse bicontinuous cubic (V_2), normal micellar cubic (I_1) and reverse micellar cubic (I_2) isotropic phases, normal micellar (rich in water , L_1) and reverse micellar (rich in oil, L_2). The high number of phases of these ternary isothermal systems is contrary to the expected less number of phases which is normally observed with polyoxyalylene block copolymers. The surfactants, and in particular nonionic, can be described as having a preferred or spontaneous mean curvature, H_0, of the polar/apolar interface, which limits the range of stable structures of a phase diagram (Svensson *et al.*, 1998).

The xylene isomer *o*-xylene was used instead of *p*-xylene in the system, L64 ($EO_{13}PO_{30}EO_{13}$) in the presence of water and the results indicate that phase behavior is insensitive to the choice of xylene isomer (Wu *et al.*, 1994).

A study of Pluronic 25R4-water-xylene gave six phases which are: two isotropic solution phases, one rich in water (L_1) and one with a high *p*-xylene-to-water ratio (L_2), and four liquid crystalline phases, a lamellar ($L\alpha$), a normal hexagonal (H_1), a reverse hexagonal (H_2) and cubic (V_2) region (Alexandridis *et al.*, 1996).

The phase behavior of surfactants is influence-limited by a “preferred” interfacial curvature (originating from the surfactant geometry) so that a ternary isothermal surfactant-oil-water phase diagram exhibits either normal (oil-in-water) or reverse (water-in-oil) phases, but usually not both. In solvent-free block copolymers, the interfacial curvature is set by the relative composition of the different blocks. A given block composition can typically result in only one type of structure; different relative block compositions are required for different structures to be formed. Homopolymers (A or B) can be used to modify the type of structure formed by A-B block copolymers (Floudas *et al.,* 1997). Floudas and company (1997) suggested that phase diagrams of ternary A-B block copolymer-A homopolymer-B homopolymer mixtures should exhibit the same general features as the ternary block copolymer water-oil phase diagram presented here.

For amphiphilic block copolymers, the curvature is set initially by the relative length of the different blocks in the copolymer but can be readily tuned by varying the degree of swelling of different blocks by respective selective solvent. This extra degree of freedom is responsible for the unique structural polymorphism observed: both “normal” and “reverse” structures can be formed at the same temperature with the same block copolymer in the presence of two solvents selective for each block (Alexandridis *et al.*, 1998).

2.8.4 Progression of Microstructures in Block Copolymer/water/oil Systems

The progression structure in the block copolymer/water/oil phase diagrams of the type discussed above can be looked at in two parts: at varying water/oil ratio and constant copolymer content and at increasing total copolymer content while keeping copolymer/oil and copolymer/water ratios constant (Alexandridis *et al.*, 1998).

An example of structure progression for the case of varying water/oil ratio at constant copolymer content is the phase sequence $L_1 \longrightarrow I_1, \longrightarrow H_1, \longrightarrow V_1, \longrightarrow L\alpha \rightarrow V_2, \longrightarrow H_2, \longrightarrow I_2, \longrightarrow L_2$ (clockwise starting from water-rich corner of the ternary phase diagram of **Figure 2.1**) observed at 40-wt% copolymer. This phase/structure is consistent with a decreasing interfacial mean curvature (H) from the left (H> 0) to the right (H< 0) side of the phase diagram, with H=0 in the lamellar phase (Fontell, K., 1990). Note that higher (>65%) copolymer concentrations are required for the V_1 and V_2 structures to form, and at such copolymer concentrations the I_1 and I_2 structures are no longer stable (Alexandridis *et al.*, 1998).

In the oil-lean part of the phase diagram (Figure 2.2), the $(EO)_{19}(PO)_{43}(EO)_{19}$ block copolymer self-assembles upon increase of its concentration into the reverse hexagonal (H_2), reverse bicontinuous cubic (V_2), and reverse micellar cubic (I_2) reverse liquid crystalline structures. The PPO content of copolymer (60%) is such that it does not favour such structures in the absence of a polar solvent. The sphere cylinder-plane sequence of structures, this time of the reverse (water-in-oil) morphology, is also observed in water lean part of phase diagram with increasing block copolymer concentration at a constant copolymer/water weight ratio, 1:4 water molecules per EO segment (Alexandridis *et al.*, 1998).

Upon an increase of copolymer concentration at constant copolymer/oil or copolymer/water ratio is a sequence of relative increase of PPO/PEO block volume fraction in the system. For a PEO/PPO block copolymer of a given block composition and molecular weight, the types of structures obtained in the presence of solvents appear to be a function of volume fraction of polar/apolar components (Alexandridis *et al.*, 1996).

Finally it is noted that the different regions in the ternary phase diagram shown in Figure 2.2 are arranged systematically around the Lα region. The lack of “mirror image” symmetry in this phase diagram is due to the nature of the PEO-water and PPO-xylene interactions (Alexandridis *et al.*, 1996).

2.9 Ternary Phase Behavior with Respect to Molecular Weight and Solvent Quality

2.9.1 Effect of Block Copolymer Molecular Weight on Phase Behavior

In block copolymer melts, an increase in copolymer molecular weight for a given A/B block composition increases the block segregation and the tendency to reorganize. The degree of segregation is proportional to N, which is a function of copolymer molecular weight. The effect of copolymer molecular weight on the self-assembly of block copolymers in the presence of selective solvents is well explained by a study of $(EO)_{19}(PO)_{43}(EO)_{19}$ and $(EO)_{13}(PO)_{30}(EO)_{13}$ block copolymers having the same, approximately symmetric (40% PEO), block composition and varying molecular weight, under the same solvent and temperature conditions (Alexandridis *et al.*, 1998).

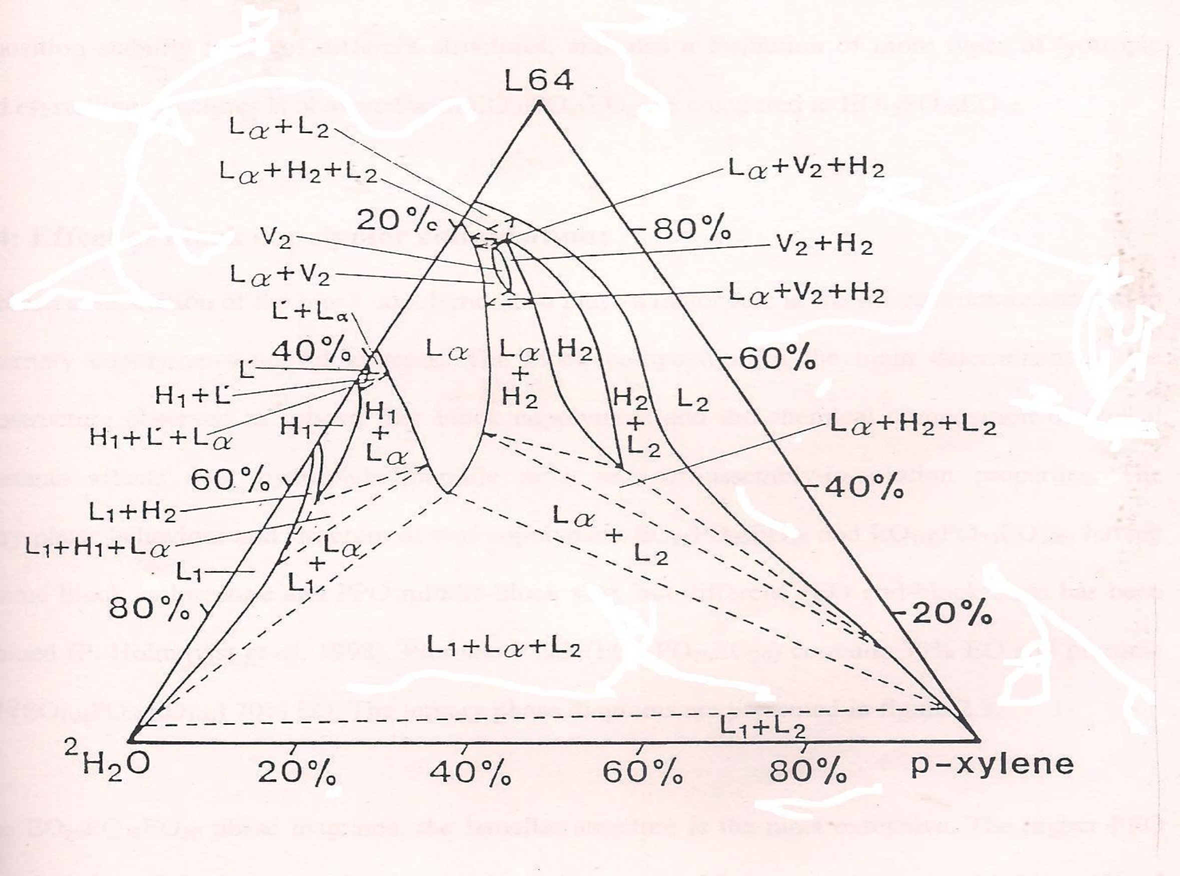


Figure 2.3 Phase diagram of $EO_{13}PO_{30}EO_{13}$ Pluronic L64-water-p-xylene ternary system at 25^0C (Alexandridis *et al.*, 1995)

Comparison of the phase diagrams given in Figures 2.1 and 2.2 confirms the trend of increasing block segregation and tendency for self-organization with increasing copolymer molecular weight, and establishes the validity of this trend in the case of PEO/PPO block copolymer self-assembly in selective solvents. The block copolymer examined in Figure 2.2 (pluronic P84), has a 45% higher molecular weight than pluronic L64 (Figure 2.3), but is of the same composition. An increase in composition stability range of different structures, and also a formation of more types of lyotropic liquid crystalline structures is observed with $(EO)_{19}(PO)_{43}(EO)_{19}$ as compared to $(EO)_{13}(PO)_{30}(EO)_{13}$ (Alexandridis *et al.*, 1998).

2.9.2 Effect of Block Copolymer Composition on Phase Behavior

Block copolymer composition also plays a major role in microstructure formation of ternary copolymer/water/oil systems. Block composition is the main determinant of the microstructure observed in solvent free block copolymers and the chemical composition of typical surfactants affects their hydrophile/lipophile ratio and self-assembly-in-solution properties. The ternary phase behavior and structure of two copolymers $EO_{20}PO_{70}EO_{20}$ and $EO_{100}PO_{70}EO_{100}$, having the same block architecture and PPO middle block size, but different PEO end-block sizes have been examined. Pluronic P123 $[(EO)_{20}(PO)_{70}(EO)_{20}]$ contains 30% EO and pluronic F127 $[(EO)_{100}(PO)_{70}(EO)_{100}]$ 70% EO (Holmqvist *et al.,* 1998). The ternary phase diagrams are presented in Figure 2.4.

In pluronic P123 phase diagrams, lamellar structure is the most extensive. The higher PEO content of pluronic F127, however, favors oil-in-water LLC structures with high interfacial curvature. No reverse LLC phases are formed by $(EO)_{100}(PO)_{70}(EO)_{100}$. Figure 2.4 shows how the increase of PEO block size affects preferred self-organization of the amphiphile block copolymers. Copolymer-water side of the $EO_{100}PO_{70}EO_{70}$ ternary phase diagrams is dominated by the micellar cubic LLC structure; significant amounts of oil are needed in order for cylindrical (H_1) and micellar microstructures to form (Holmqvist *et al.*, 1998).

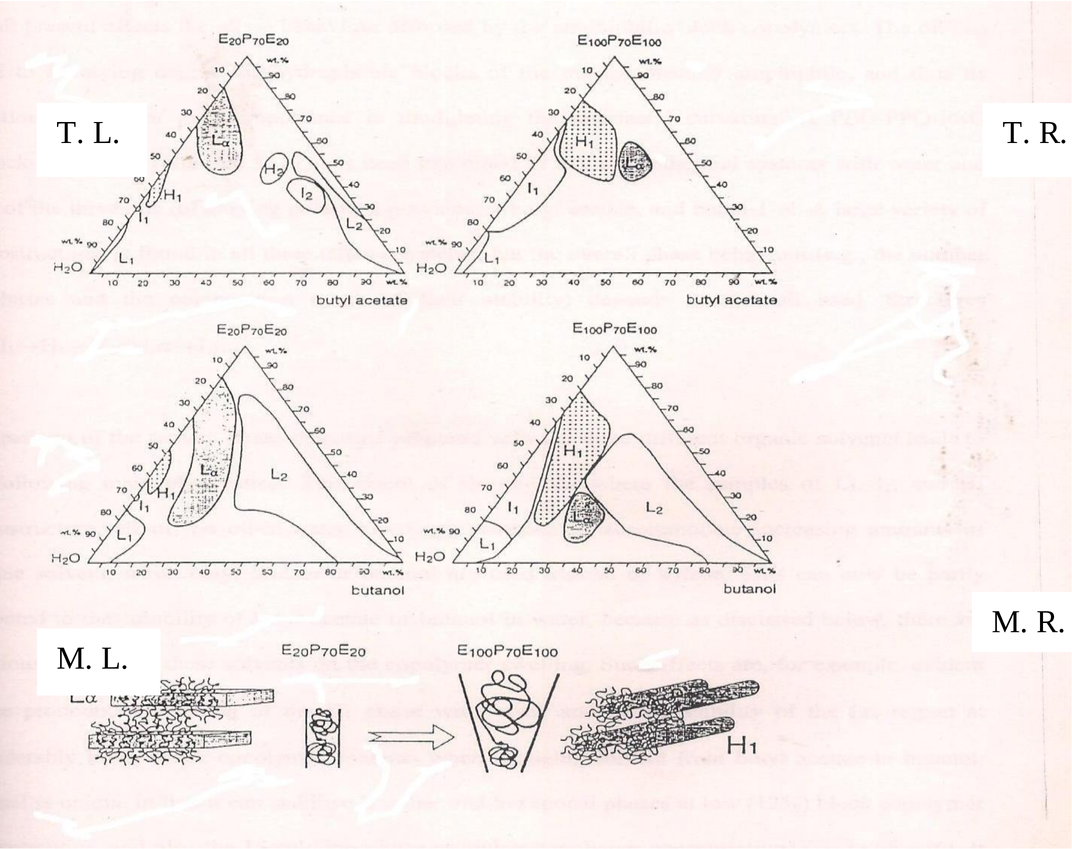


Figure 2.4 Phase diagrams of $EO_{20}PO_{70}EO_{20}/D_2O$/n-butyl acetate (T. L.), $EO_{20}PO_{70}EO_{20}/D_2O$/ butan-1-ol (M. L.), $EO_{100}PO_{70}EO_{100}/D_2O$/n-butyl (T. R.) and $EO_{100}PO_{70}EO_{100}/D_2O$/ butan-1-ol (M. R.) (Holmqvist *et al*., 1998).

B. L. B. R.

Kipkemboi and coworkers (2003) showed that even though the triblock copolymers; $EO_{17}PO_{59}EO_{17}$ and $EO_4PO_{59}EO_4$ have similar hydrophobic middle block, their ternary systems with deuterated water and xylene have different phase structures. The isothermal phase diagram of $EO_{17}PO_{59}EO_{17}$-D_2O-xylene exhibited a nearly identical phase diagram with $EO_{27}PO_{61}EO_{27}$-D_2O-xylene (Svensson *et al*., 1998).

2.9.3 Effect of Solvent Quality on Phase Behavior

The quality of the solvent and its ability to swell the different blocks will affect phase behavior and structure (Holmqvist *et al.*, 1997). By adding variations in solvent quality, that is, whether the solvent is a good, marginal, poor, or non-solvent for blocks A, B or C in block copolymers ABA, BAB and ABC where A, B, C are surfactant polymer blocks, together with external variables such as temperature and pressure, the resultant interactions are complex enough that qualitative theories have been developed to a limited extent (Benjamin, 1995).

An important issue in understanding of self-assembly is on how the nature of oil present affects phase behavior afforded the amphiphile block copolymers. Oil can swell to a varying degree the hydrophobic blocks of the macromolecular amphiphile, and thus its selection will be of great importance in modulating the interfacial curvature. PEO-PPO-PEO tri-block copolymers $EO_{20}PO_{70}EO_{20}$ and $EO_{100}PO_{70}EO_{100}$ have been examined in ternary isothermal systems with water and each of the two oils of varying polarities; n-butyl acetate and butan-1-ol. Isothermal diagrams of ternary phase diagrams are presented in Figure 2.4. A large variety of microstructures is found in the two ternary systems, but the overall phase behavior, for example, the number of phases and composition range of their stability depends on oil used. The structures are L_1, I_1, H_1, V_1, $L\alpha$ and L_2 (Holmqvist *et al.*, 1998).

Composition of the ternary phase diagrams prepared with two different organic solvents leads to the following main observation. The extent of the regions where the samples of L_1, I_1, and H_1 microstructures, all of which are of oil-in-water topology, increases to accommodate increasing amounts of organic solvent, when butyl acetate or butanol is used. $EO_{20}PO_{70}EO_{20}$-water-butyl acetate ternary system forms five lyotropic liquid crystalline phases (I_1, H_1, Lα, H_2, I_2) with little swelling as compared to three of $EO_{20}PO_{70}EO_{20}$-water-butanol which show high swelling. These effects are evident in the pronounced swelling of the H_1 phase with water and in stability of the Lα region at considerably lower copolymer contents when changing solvents from butyl acetate to butanol (Holmqvist., *et al*., 1998).

Butanol is unique in that it can stabilize lamellar and hexagonal phases at low (20-wt %) block copolymer concentrations, and also the L_2 solution phase at high copolymer concentrations (up to 60-wt%). It thus acts in a manner comparable to cosurfactant known from systems containing low molecular weight amphiphiles. The normal hexagonal and the lamellar regions in the cases of butyl acetate are stable at copolymer concentrations above 45-wt%. Up to 30-wt% butyl acetate can be accommodated in the normal hexagonal structure.

The stability of cubic structure from 20-wt% to 60-wt% copolymer concentration range and its ability to stabilize significant amounts of butanol and butyl acetate are notable, given the practical applications that such as cubic gels are finding. Given the same ternary composition and structure, the lattice spacing was found to decrease, as the oil became less hydrophophilic, that is, from butyl acetate to butanol. This trend was observed in both normal hexagonal and lamellar regions, which suggested the location of oils (Holmqvist *et al*., 1998).

Phase behavior $EO_{27}PO_{61}EO_{27}$-water-*p*-xylene ternary system was investigated by Svensson and coworkers (1998) and its isothermal phase diagram presented in Figure 2.5. The ternary system gave six lyotropic liquid crystalline phases which were I_1, H_1, $L\alpha$, V_2, H_2 and I_2. There were also the two isotropic liquid solutions water-rich normal micellar solution (L_1) and water-lean reverse micellar solution (L_2).

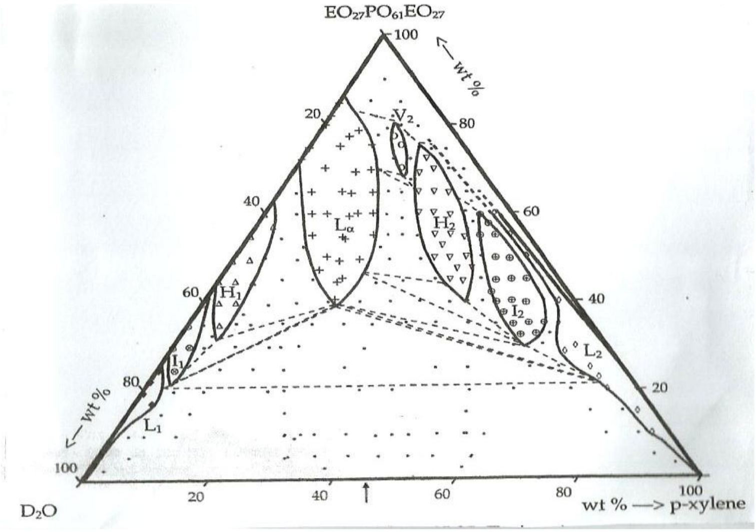


Figure 2.5 Isothermal phase diagram of P104/water/*p*-xylene ternary system at 25 ^{0}C (Svensson *et al*., 1998)

2.10 Physicochemical Properties of Surfactants

Physico-chemical investigations of surfactants in aqueous solutions with or without cosolvents are important in understanding the nature and mechanism of intermolecular interactions in these systems. Studies of physico-chemical properties of aqueous solutions of surfactants, their relevance in biological systems and their intriguing and fascinating features continuously provide new challenges to the scientific community. These properties are of significant importance especially on issues to do with enhanced oil recovery, detergency and concentration of ores by froth floatation in metallurgical processes (Sansanwal, 2006).

Physico-chemical properties of an aqueous solution of mixed surfactants is found to change with increase in surfactant concentration in the way aggregates form. A mixture of surfactants forming insoluble aggregates and mixed micelles has become very important in industrial applications and surface chemical work of surfactants because of the tendency to form aggregated structures which are very different from those formed by solutions which have pure solutions. Infact, some phenomena, which are not expected to occur in pure solution systems do occur in aqueous solutions containing mixtures of surfactants (Satan and Sawant, 2006).

In the uses of surfactants and polymers individually or in mixtures in physico-chemical processes, physicochemical properties such as cloud points indicate the limit of their solubility. Therefore, determination of cloud points is very important physico-chemical exercise in judging the quality and characteristic of a surfactant/polymer before use in a process especially where elevated temperature prevails (Soumen and Moulik, 1999).

2.10.1 Cloud Point

2. 10.1.1 Cloud Point of Nonionic Surfactants

Aqueous micellar solutions of nonionic surfactants are strongly affected by variations in temperature and concentrations. The isotropic single micellar solution separates into a diluted and a concentrated micellar solution when temperature is raised. The balance between hydrophilic/hydrophobic interactions is the most likely cause that determines the temperature at which this phase separation occurs. Nonionic surfactants change from water-soluble to oil soluble with increasing temperature. This behavior is used to purify the substances. The temperature at which this occurs is known as the cloud point (CP) (Gu and Galera, 1999). Therefore, CP is the temperature above which surfactant phases separate and precipitate from solution (Na *et al.*, 1999a).

Nonionic surfactants with poly(ethylene oxide) (PEO) chains as the hydrophilic moiety are used frequently in pharmaceutical formations. Some of them are effective solubility enhancers for poorly soluble drugs and some are strong dispersants and colloid stabilizers used in emulsion and suspension dosage forms. This type of nonionic surfactants has a unique property which is the display of CP. A study of cloud points of a variety of nonionic surfactants has shown them to increase with the hydrophile-lipophile balance (HLB) (Schott, 1969).

Cloud point is very sensitive to the presence of additives even at very low concentrations. Additives are said to modify the surfactant-solvent interactions and as a result they change the CMC, the size of the micelles and the phase behavior in the surfactant solutions. CP of a dilute nonionic surfactant solution increases upon addition of ionic surfactant. Incorporation of an ionic surfactant into nonionic surfactant micelles introduces electrostatic repulsion between the micelles thus hindering coarcervate phase formation and therefore raising CP. Since nonionic surfactants are used as solubilizers, emulsifiers and detergents in many industrial processes, cloud point data are of great interest for example the solubility of oil-water emulsions stabilized by nonionic surfactant is related to cloud point (Schamehorn, 1986).

2.10.1.2 Effect of Inorganic Salts on Cloud Point of Nonionic Surfactants Solutions

Schott and Han (1977) in their study on the effect of inorganic salts on CP considering the contributions of cations and anions, they noted that the effect of anions followed the order of Holfmeister series, that is, anions that break the water structure, such as I^-, $[Fe(CN)_5NO]^{2-}$, and SCN^-, boost the cloud point whereas those that promote the water structure or bind water molecules extensively, such as OH^-, F^-, Cl^-, SO_4^{2-}, and PO_4^-, suppress the cloud point. For cations, they proposed that most divalent and trivalent cations, together with H^+, Ag^+, and Li^+, boost the cloud point by forming complexes with either groups of PEO chain. But cations such as Na^+, K^+, Cs^+, and NH_4^+ do not form such complexes and suppress CP by dehydration.

In developing liquid formulations containing a nonionic surfactant, CP of a surfactant can be a key parameter for consideration. Phase-separation for the surfactant under elevated temperatures, such as that encountered in steam sterilization of parenteral products, often leads to content heterogeneity. In the case of dispersed dosage forms, phase-separation of the surfactant can result in physical instability of the dispersion (Na *et al.*, 1999a). Conversely, a surfactant phase change could be utilized beneficially in pharmaceutical formulations. An example is the gelation of poloxamer solutions and its potential applications in the controlled-release of drugs through various routes of delivery (Stratton *et al.*, 1997).

In modulating CP, it appears easier to lower it than to raise it. Many common salts such as sodium chloride are very effective CP suppressors. A few salts such as those containing I^-, $[Fe(CN)_5NO]^{2-}$, and SCN^-, anions can raise the CP, but they are likely to be toxic and unsuitable for use in pharmaceutical formulations. It has been observed that presence of an electrolyte at high concentrations is likely to affect electrostatic stabilization of colloids and is detrimental to the physical stability of dispersed dosage forms (Na *et al.*, 1999b).

Soumen and Moulik (1999) found that CP of binary mixtures of nonionic surfactant Brij 56 with polymers polyvinyl alcohol (PVA) and methyl cellulose (MC) depend mildly on concentration and PVA has a very mild effect on the CP of Brij-56.

CMC of nonionic surfactants C_8E_6, $C_{10}E_6$ and $C_{12}E_6$ is raised by adding of inorganic salts Na_2SO_4, $NaIO_3$, NaCl, NaBr, $MgCl_2$ and LiCl but lowered by adding NaI and NaSCN respectively. CMC raising means salting-out effect of hydrocarbon moiety (Nagamune *et al.*, 1977).

2.10.2 Micelle Formation

Surfactants are amphiphilic molecules that contain a nonpolar segment (tail) and a polar segment (head). Because of this characteristic, surfactants form aggregates when they are dissolved in polar solvents such as water. At low concentrations, the surfactant exists as individual entities but as the concentration of the surfactant increases the molecules tend to associate to form aggregates. The aggregation number indicates how many molecules are present in an aggregate and in most cases, this is a rather narrow size. In aqueous solutions, the hydrophobic tails of the surfactant associate, leaving the hydrophilic head groups exposed to the solvent. The simplest of these aggregates that have an approximately spherical shape are called micelles and the process through which they form is called micellization. The transition from a monomeric solution to an aggregated form can be seen as a change in the slope of plots against surfactant concentration of many physical properties (e.g., viscosity, conductance, surface tension). The concentration at which this change takes place is called the critical micelle concentration (CMC) (Flores *et al.*, 2001).

In nonpolar solvents, the hydrophilic segment gets poorly solvated and therefore the hydrophilic heads form the interior of the aggregates while the hydrophobic tails surround the polar core and are responsible for the solubility of the aggregates. This leads to formation of two structures which are called normal and reverse micelles. Micelles are structures in which the hydrophobic portions of the surfactant molecules associate together to form regions which the solvent is excluded. Micelles have an important behavior in that they act as sites for the dissolution of lipophilic (fat-soluble) molecules, a property known as solubilization. Solubilization is characterized by a dramatic increase in of solubility the lipophilic material above the CMC. This is used as a means of detecting onset of micellization but there is a problem of the lipophilic material influencing CMC by supporting or opposing aggregation process (Hunter, 1987).

The role played by solvent in micelle formation is largely responsible for the self-organization on amphiphilic molecules into micelles and liquid crystals (Callaghan *et al.*, 1993). Micelle or liquid crystal formation has been reported to occur in solvents such as ethylene glycol (Ray and Nemethy 1969), glycerol (Yamaguchi *et al.*, 1987), formamide (Rico and Lattes, 1986) and hydrazine (Ramadhan *et al.*, 1983) where all these solvents have high cohesive energies, dielectric constants and a high degree of hydrogen bonding. The ability of a solvent to form hydrogen bonding is a necessary condition for micelle formation (Beeslay *et al.*, 1988). However, micelle formation has been reported in solvents such as acetone, acetonitrile and dimethylsulfoxide (Gopal, 1973) which have very little or no hydrogen bonding at all.

2.10.2.1 Critical Micelle Concentration

Due to the nature of monomer–micelle equilibrium, the CMC is not properly defined but it is a transition region over a small composition range. CMC is a transition region over a small composition range and therefore its exact determination is difficult. Experimentally, the data obtained from measurements of physic-chemical properties when plotted versus surfactant concentration, can be used to estimate CMC by getting where there is a break of the curve. The CMC of a surfactant in a given solvent is thus of great help in understanding and predicting behavior (Flores et al., 2001). Above CMC, surfactant solutions have the ability to solubilize otherwise insoluble organic material by incorporating it into the interior of micelles (Shaw, 1989).

2.10.2.2 Micellization in Block Copolymer Surfactants

In a certain temperature range and at a certain copolymer concentration, PEO–PPO–PEO block copolymers of suitable composition and molecular weight form polymolecular aggregates (micelles) in an aqueous environment. Micelle formation can be induced by temperature. For example, L64 in water forms unimers at low temperature (about 6 ^{0}C) because water is a good solvent for both PEO and PPO. With an increase in temperature, the solvent quality of water with PPO becomes poorer and micelles are formed. The formation of triblock copolymer micelles is extremely temperature dependent and this leads into a dramatic decrease of CMC upon a small increase in temperature. This arises due to temperature dependent difference in solvation of the ethylene oxide (EO) and propylene oxide (PO) blocks (Mata *et al*., 2004).

Micelles can also be formed by changing solvent quality of the PEO blocks in L64. L64 is soluble in o-xylene and by addition of water, which is not miscible with xylene, the water molecules interact with PEO and thus change the solvent quality of the hydrated PEO. Only surfactant monomers contribute to surface and interfacial lowering and dynamic phenomena, such as wetting and foaming, which are governed by the concentration of free monomers in the solution. Micelles may be seen as a reservoir for surfactant monomers (Rosen, 1978).

In the study of $(EO)_{78}(PO)_{30}(EO)_{78}$ aqueous solutions showed a transition at the critical micellization temperature (CMT), below which a small particle size of unimers (2.3 nm) is observed with very little temperature dependence. Micelle formation becomes appreciable above the CMT. In the micelle region, the measured micellar mass is found to increase linearly with temperature, while the hydrodynamic radius of the micelles remains nearly constant (8.0 nm). In the case of $(EO)_{13}(PO)_{30}(EO)_{13}$, detectable aggregates start to be observed at 25 ^{0}C when the concentration is above approximately 6%. The micelle size increases with concentration (10 nm at 8% to 12.5 nm at 20%) and exhibits significant polydispersity. At 35 ^{0}C, however, invariant values for the hydrodynamic radius are found over a wide concentration range and the micelles are roughly monodisperse (Al-Saden, *et al.*, 1982).

Aggregation of triblock copolymers when mixed with water is observed to be sensitive to the presence of many additives. Observations made from a series of investigations on aggregation of triblock copolymers in water show that the presence of electrolytes, such as NaCl and NaF cause a decrease in CMC and CMT values and this is termed as salting-out while electrolyes such as NaI, NaCNS together with nonelectrolytes such as small-chain alcohols and urea cause an increase in both CMC and CMT values, a process called salting-in. The PEO–PPO–PEO triblock polymers are known to interact with ionic surfactants, which are often used in the processing of various triblock copolymer formulations in several industries (Mata *et al*., 2004)

2.10.3 Effect of Added Inorganic Salts on Micelle Formation of Nonionic Surfactants

The critical micelle formation (CMC) of nonionic surfactants in aqueous solutions is lowered by addition of most inorganic salts. This is due to fact that salts bring about the dehydration of the hydrophilic moiety of the surfactant monomer causing the enhancement of the tendency towards micelle formation, that is, CMC lowering. The micelle formation (CMC) is determined by the balance of surfactant stability between that in the monomer and that in the micelle state. Salts have influence not only on the dissolved state of the monomers, but also on that of micelles in solution, and so the dehydration mechanism has been questionable. Salts exhibiting salting-out or salting-in on oxyethylene groups give an increased or decreased solubilizing power respectively with the salt concentration as compared with that in the salting-free solution (Nagamune, 1977).

2.10.4 Determination of CMC

Experimentally, CMC is found by plotting a graph of a suitable physical property as a function of surfactant concentration. An abrupt change of slope marks the CMC. Choice of CMC is never unambiguous, since the change in slope occurs over a more or less narrow range of concentrations, whose magnitude depends on the physical property being measured and sometimes on the nature of data and on the way they are plotted. Thus CMC determinations are usually on the basis of sharp change in the colligative properties like clouding, surface tension, iodine solubilization technique, conductivity e.t.c (Jadhav, *et al*., 2012).

CHAPTER THREE

MATERIALS AND EXPERIMENTAL

3.1 Materials and Sample Preparation

Triblock copolymers $(EO)_{27}(PO)_{61}(EO)_{27}$ (Pluronic P104) and $(EO)_6(PO)_{34}(EO)_6$ (Pluronic L62) were both obtained from BASF corp. U.S.A and were used as received. The copolymers have nominal weights of 5900 and 2500 respectively and approximately 40-wt% and 20-wt% of PEO blocks respectively. These molecular weights and compositions correspond to 54 ethylene oxide, and 61 propylene oxide segments for P104 and 12 ethylene oxide and 34 propylene oxide segments for L62 respectively. Polyoxyethylene (20) stearyl ether (Brij-78) having the composition $\{C_{18}H_{37}(OCH_2CH_2)_nOH\}$ was obtained from Aldrich chemical company and was dried at 120 ^{0}C to remove all the dissolved water.

Deuterated water H_2O (99.80 atom % ^{2}H) was purchased from Dr Glasser AG, Basel, Switzerland while benzyl alcohol of purity 99.0% was obtained from Fluka chemie AG, Bushs, Switzerland. At 25 ^{0}C the density of the deuterated water is 1.11044 g/mL. This density was used to calculate volume fractions from weight fractions.

Triton X-114 (TX-114) was received from Fluka chemie AG Switzerland, Sodium Dodecyl Sulphate (SDS) which was 99.5 wt% was obtained from E. Merck Germany and Cetyl Trimethyl Ammonium Bromide was received from Sigma-Marich, U.S.A. All the above chemicals were used without further purification. The inorganic salts, Sodium Chloride, Sodium Sulphate and Aluminium Chloride were of laboratory reagent grade and they were dried at 110 ^{0}C for 6 hours before use.

Structural formulae of the compounds used in this study are: Pluronic L-62 $(EO)_6$-$(PO)_{34}$-$(EO)_6$, Pluronic P-104 $(EO)_{27}$-$(PO)_{61}$-$(EO)_{27}$, Brij-78 or polyoxyethylene (20) stearyl ether [$C_{18}H_{37}(OCH_2CH_2)_nOH$; n=20], Triton X-114 R'-C_6H_4-$(OC_2H_4)_{7.5}$-OH, where R is a branched octyl group and n is the average number of the ethylene oxide groups.

3.2 Determination of Phase Behaviour of Ternary Systems: P104/D_2O/Benzyl Alcohol and L62/D_2O/Benzyl Alcohol

3.2.1 Sample Preparation

Samples of the two surfactants, L-62 and P-104, were prepared individually by weighing appropriate amounts in analytical balance each of them separately from 1.0 gram to 9.0 grams. The weighted samples were put into glass bottles in which D_2O and Benzyl alcohol were added after measuring appropriate quantities to give a mixture total of 10.0 grams in the tubes. These sample bottles were stoppered immediately to be run in a centrifuge machine. The samples were repeatedly centrifuged over two days each to facilitate proper mixing.

3.2.2 Preparation and Identification of Lyotropic Liquid Crystalline Mesophases

After preparation, the samples were put in a centrifuging machine and the machine set to run at 70 revolutions per second for 2 hours repeatedly for each sample to ensure proper mixing. The equilibrated samples were examined by visual inspection in normal light and between polarizers to check for phase separation, homogeneity and birefrigency. One-phase samples are macroscopically homogenous. Anistropic phases can be recognized from their optical birefrigence. Further analysis and structural characterization of the lyotropic liquid crystalline phases obtained was done by employing small-angle X-ray scattering (SAXS). SAXS measurements were performed on a Kratky compact small-angle X-ray camera equipped with Cu Kα radiation of 1.542 Å operating at 50 kV and 40 mA, details of which have been given elsewhere (Kipkemboi *et al*., 2003). All SAXS measurements were performed at 25 ^{0}C. SAXS measurements were carried out in the Department of Physical Chemistry 1, counter for Chemistry and Engineering, Lund University, Sweden by Katarina Flodström.

3.2.3 Construction of Isothermal Ternary Phase Diagrams

Isothermal ternary phase diagrams for each of the ternary systems were drawn using Gibbs triangle. On the Gibbs triangle, which is an equilateral triangle, the three pure component substances are represented at the corners, *A*, *B*, and *C*, as shown in Figure 3.1. Because of its unique geometric characteristics, an equilateral triangle provides the simplest means for plotting ternary composition. In the figure, each apex represents one of the components, which were; block copolymer, water and benzyl alcohol respectively. Here, the sides of the triangle .represent the three binary systems, while the inside of the triangle presents all the three components (Campbell, F.C., 2012)

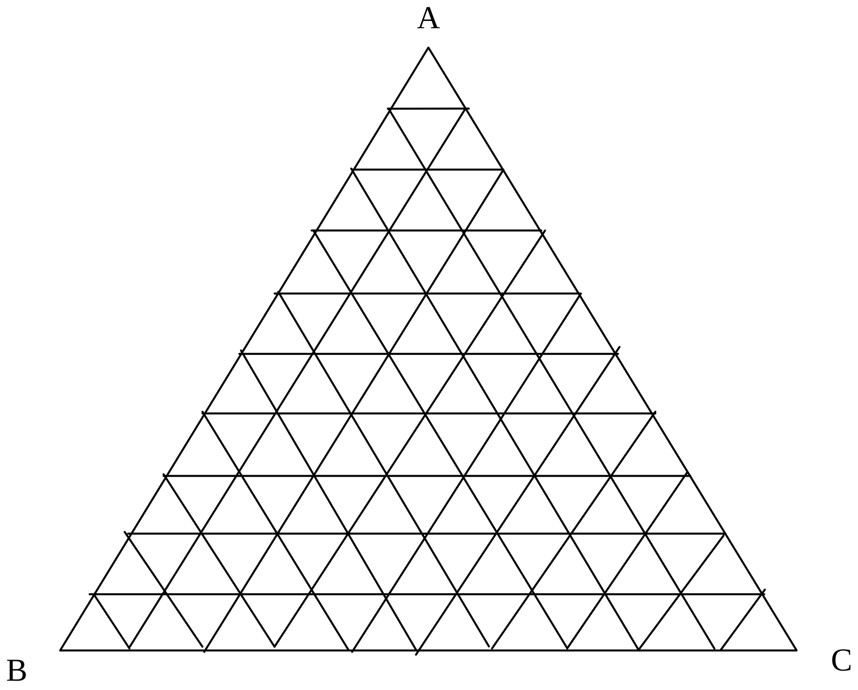


Figure 3.1 Gibbs Triangle for isothermal ternary phase diagram construction (Campbell, F.C., 2012)

3.3 Critical Micelle Concentration (CMC)

In aqueous solutions, the hydrophobic tails of the surfactant associate, leaving the head groups (hydrophilic) exposed to the solvent. The simplest of such aggregates, with an approximately spherical shape, are called micelles. The transition from a monomeric solution to an aggregated form can be seen as a change in the slope of plots against surfactant concentration of many physical properties (e.g., viscosity, conductance, surface tension). The concentration at which this change takes place is called the critical micelle concentration (CMC) (Flores *et al*., 2001).

Plots of concentration against the measured physico-chemical property were made and used to estimate CMCs of the solutions.

3.4 Cloud Point of the Nonionic Surfactants

3.4.1 Procedure for Determination of CP

The cloud point is normally determined by using a volume of surfactant which is transferred to a clean and dry glass tube. This sample is warmed in a water bath and stirred carefully with a thermometer. The solution becomes turbid at the cloud point. At this temperature, heating is controlled and the temperature raised to about 5^0C above cloud temperature. Heating is stopped and the sample cooled slowly without removing the tube from the hot water bath. Turbid mixture becomes clear at cloud temperature. This procedure is repeated for two additional times. Carefully controlled experiment should give reproducible results (Khan, A. 1999).

3.4.2 Determination of CP of solutions of L-62, P-104 and Brij-78

Pure sample solutions of L62, P104 and Brij-78 surfactants were prepared individually by weighing appropriate quantities to prepare stock solutions of 1.0 molL^{-1} each surfactant in 100mL volumetric flasks. The concentrations of each surfactant solution were then varied from 0.001molL^{-1} to 1.0 molL^{-1} by specific volumes of stock solutions and diluting them with distilled water to desired concentrations. CP of each dilute solution was determined by warming the solutions in boiling tubes while stirring carefully with a thermometer until the solutions became turbid. The temperature was noted and heating was continued such that temperature was raised slightly to 5 ^{0}C above the cloud temperature. Heating was stopped and samples were cooled without removing sample tubes from the hot water bath. The temperatures at which turbid solutions became clear were noted as this indicated cloud points.

The procedure was done for surfactants solutions in mixtures with inorganic salts: sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and aluminium chloride ($AlCl_3$). Other solution mixtures used include those of ionic surfactant additives SDS and CTAB and the nonionic surfactant additive TX-114.

Cloud points obtained in each case were plotted against concentrations of surfactants, inorganic salts added, ionic surfactants added and the wt % of nonionic surfactant used. From the curves obtained CMCs of solutions were estimated from points of change of gradient of the curves and recorded.

3.5 Measurement of Specific Conductivity of Solutions of L62, P104 and Brij-78

Pure sample solutions of L62, P104 and Brij-78 surfactants were prepared individually by weighing appropriate quantities to prepare stock solutions of 1.0 $molL^{-1}$ of each surfactant in 100ml volumetric flasks. These stock solutions were used to make solutions of varying concentrations from 0.001 $molL^{-1}$ to 1.0 $molL^{-1}$ by diluting them with distilled water to appropriate volumes to make the desired concentrations. Specific conductivities of these solutions were measured by use of a conductivity meter at 25 ^0C while varying the concentration of surfactants. The tip of the conductivity meter was cleaned after dipping into the respective solutions before it was used again in another solution. This process was repeated for all the solutions of pure surfactants and results recorded.

Sample solutions of surfactants with inorganic salts were prepared by weighing appropriate quantities of the salts into 1.0 wt% surfactant solutions and their specific conductivities determined by use of a conductivity meter. The salts that were used are sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and Aluminiun Chloride ($AlCl_3$) respectively. The procedure was repeated for all solutions of varying salt concentrations and the specific conductivities obtained recorded. Concentrations of the respective salts were plotted against specific conductivity of the solutions.

Sample solutions of surfactants with ionic surfactant additives, SDS and CTAB, were prepared by weighing appropriate quantities of the ionic surfactant into 1.0 wt % surfactant solutions to make varying concentrations of these ionic surfactants in the mixture. Specific conductivities of these solutions were determined by use of a conductivity meter and recorded. Concentration of ionic surfactant additives were plotted against specific conductivity to give the general change in specific conductivity as concentration of the ionic surfactant increased.

Sample solutions containing surfactants; L62, P104 and Brij-78 with nonionic surfactant TX-144 were prepared by increasing the concentration of TX-114 while decreasing the concentration of the respective nonionic surfactant so as to maintain total quantity of mixed surfactants in solution. Specific conductivities of these solutions were determined by use of a conductivity meter and recorded. The concentration of TX-114 in solution was plotted against the specific conductivity.

3.6 Measurement of Relative Viscosity

Pure sample solutions of L62, P104 and Brij-78 surfactants were prepared individually by weighing appropriate quantities to prepare stock solutions of 1.0 $molL^{-1}$ each surfactant in 100ml volumetric flasks. These samples solutions were used to make solutions of varying concentrations from $0.001molL^{-1}$ to $1.0molL^{-1}$ by diluting them with distilled water to appropriate volumes to make the desired concentrations. Relative viscosities of these solutions were measured by use of a viscometer. This procedure was repeated for all the solutions of pure surfactants and results recorded.

Sample solutions of surfactants with inorganic salts were prepared by weighing appropriate weights of the salts into 1.0 wt % surfactant solutions and their relative viscosities determined by use of a viscometer. The salts that were used are sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and Aluminiun Chloride ($AlCl_3$) respectively. The procedure was repeated for all solutions of varying salt concentrations and the relative viscosities obtained recorded. Concentrations of the respective salts were plotted against relative viscosity of the solutions.

Sample solutions of surfactants with ionic surfactant additives, SDS and CTAB, were prepared by weighing appropriate weights of the ionic surfactant into 1.0 wt %

surfactant solutions to make varying concentrations of these ionic surfactants in the mixture. Relative viscosities of these solutions were determined by use of a conductivity meter and recorded. Concentration of ionic surfactant additives were plotted against relative viscosity to give the general change in relative viscosity as concentration of the ionic surfactant increases.

Sample solutions containing surfactants; L-62, P-104 and Brij-78 with nonionic surfactant TX-144 were prepared by increasing the concentration of TX-114 while decreasing the concentration of the respective nonionic surfactant so as to maintain total quantity of mixed surfactants in solution. Relative viscosities of these solutions were determined by use of a viscometer and recorded. The concentration of TX-114 in solution was plotted against the relative viscosity.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Phase and Structure Behavior of Ternary Systems

A novel development in the field of amphiphilic block copolymers is the discovery that ternary isothermal systems consisting of a PEO/PPO block copolymer, "water", and "oil" (where "water" and "oil" are selective solvents for the PEO and PPO blocks, respectively) can exhibit a very rich structural polymorphism where self-assembled phases such as lyotropic liquid crystalline phases are formed (Holmqvist *et al.*, 1997).

The self assembled lyptropic liquid crystals are best presented in an isothermal ternary phase diagram by use of a Gibbs triangle (Campbell, 2012). The different lyotropic liquid crystalline phases so far formed are: lamellar (L_α), normal hexagonal (H_1), reverse hexagonal (H_2), normal bicontinous cubic (V_1), reverse bicontinous cubic (V_2), one with high oil/water ratio; normal micellar cubic (I_1), and one with high water/oil ratio; reverse micallar cubic (I_2) and two solutions, L_1 and L_2 which denote water-rich (normal micellar) and water-lean/oil-rich (reverse micellar) solutions (Alexandridis *et al.*, 1998).

4.2 Phase Behavior and Structure of P104 and L62 in water and benzyl alcohol.

The different phases of ternary systems comprising of P104/D_2O/benzyl alcohol and L62/D_2O/benzyl alcohol at 25 ^{0}C were determined and presented in isothermal ternary phase diagrams in Figures 4.1 and 4.5.

4.2.1 Phase Behavior and Structure of P104/D_2O/Benzyl Alcohol ternary system

The polymer has about 60% PPO and therefore asymmetric in PEO-PPO composition. Since it has a fairly higher percentage of PEO block molecular weight, it is likely to crystallize at low temperature. Isothermal phase diagram of P104/D_2O/Benzyl Alcohol ternary system at 25 ^{0}C is presented in Figure 4.1.

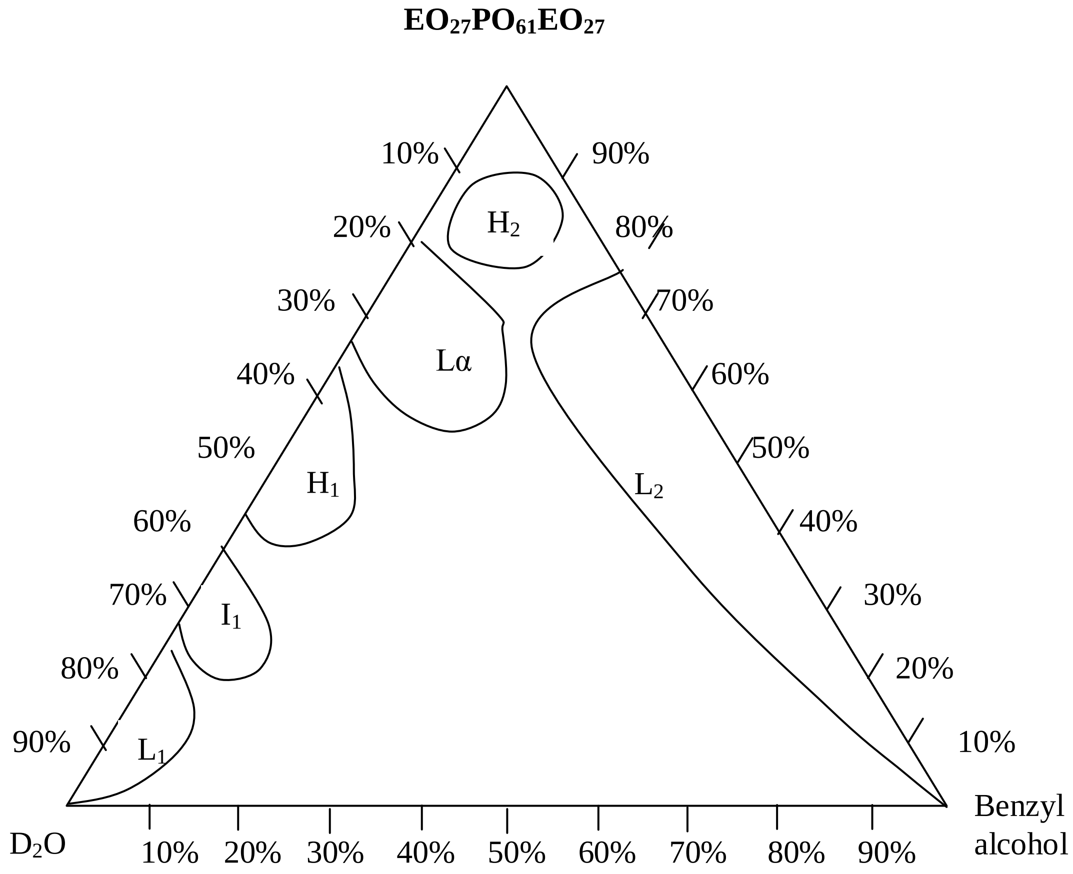


Figure 4.1 Isothermal phase diagram of P104-D_2O-benzyl alcohol ternary system at 25 ^{0}C.

Solid lines indicate boundaries of one-phase regions. Samples whose compositions fall outside the one-phase regions are dispersions of two or three phases (depending on the location in the

phase diagram) (Svensson *et al.*, 1998). In this system, four different lyotropic liquid crystalline phases were obtained, which were identified as follows starting from the water axis and progressing clockwise over the oil corner: normal micellar cubic (l_1), normal hexagonal phase (H_1), lamellar ($L\alpha$) and reverse hexagonal (H_2) as well as two isotropic solution phases, one water rich (normal micellar – L_1) and one water lean (reverse micellar – L_2) as seen in Figure 4.1. This system gave less number of lyotropic liquid crystalline phases as compared to those given by the P104/water/p-xylene (six lyotropic crystalline phases) Figure 2.4 (Svensson *et al.*, 1998).

This structural phase sequence is consistent with a decreasing interfacial curvature (H) from left (H>0) to the right (H<0), with H=0 in the lamellar phase. This modulation of the interfacial curvature (and the resulting structure) is due to the ability of the macromolecular blocks to swell to a varying extent depending on the amount of the solvent available (Fontell, K., 1990).

4.2.1.1 Normal Micellar Cubic Liquid Crystalline Phase ($l_{1)}$

As the polymer concentration increases, micelles crystallize into a cubic lattice and the L_1-I_1 phase transitions are easy to detect with the eye since the cubic phases are more viscous. Macroscopically samples in a one phase normal micellar (I_1) or reverse micellar (I_2) regions are very stiff with a clear glassy appearance, and they are optically isotropic (non-birefregent) gels (Kipkemboi *et al.*, 2003). A small homogenous one-phase normal micellar cubic region was found in the P104-water-benzyl alcohol ternary system along the copolymer-water axis between the normal micellar solution (L_1) and the normal hexagonal region (H_1). This normal micellar cubic structure forms over a more limited copolymer range of 18 wt% to 24 wt% at 25 ^{0}C and swells up to 11 wt% of benzyl alcohol. The location of this cubic phase in the ternary phase diagram suggests that it is composed of normal micelles that have crystallized into a cubic lattice.

A SAXS diffraction pattern typical of samples in the l_1 region for the $EO_{27}PO_{61}EO_{27}/D_2O$/benzyl alcohol is presented in Figure 4.2. A total of four Bragg peaks were identified, which can be indexed as the *hkl*=111, 220, 311 and 422 reflection of a face centred space group, Fd3m (Q277), characterized by Bragg reflections whose reciprocal spacing follow the relationships $\sqrt{3}$, $\sqrt{8}$, $\sqrt{11}$, $\sqrt{24}$. These four reflections in the cubic phase were found to be consistent with the first, second, third and sixth reflections in the Fd3m space group (Kipkemboi *et al.*, 2003). There was no reverse isotropic liquid crystalline phase observed in this ternary system unlike in the P104-water-*p*-xylene case as shown in Svensson *et al.*, 1998.

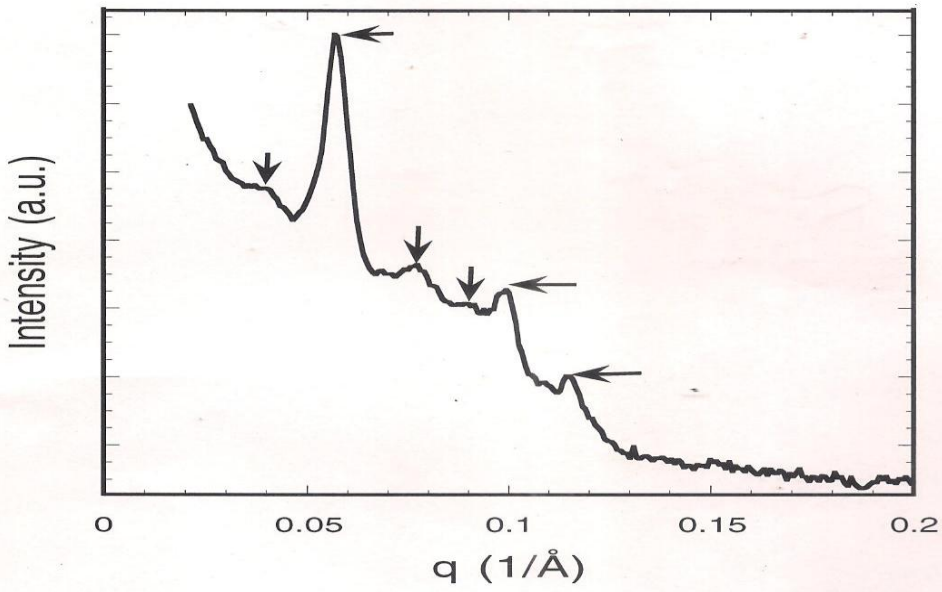


Figure 4.2 A SAXS diffraction pattern of samples in the l_1 region for the P104/D_2O/benzyl alcohol ternary system at 25 ^{0}C.

4.2.1.2 Normal and Reverse Hexagonal Liquid Crystalline Phases (H_1 and H_2)

Samples in hexagonal regions are relatively stiff, transparent and optically birefringent (anistropic). Normal hexagonal phase was observed to occur along the binary water-P104 axis between copolymer compositions 22 wt% and 57 wt% and swells up to 11 wt% of benzyl alcohol. Reverse hexagonal phase (H_2) occurred along the binary axis benzyl alcohol- P104 and between 73 wt% and 87 wt% copolymer with a maximum water content of about 27 wt%. Figure 4.3 shows a SAXS diffraction pattern typical of samples belonging to the H_1 domains which were investigated in this study. Relative position of the Bragg reflections, 1:√3:√4:√7 were found to be consistent with the two dimensional hexagonal order and they indeed confirmed the two-dimensional hexagonal structure (Kipkemboi *et al*., 2003).

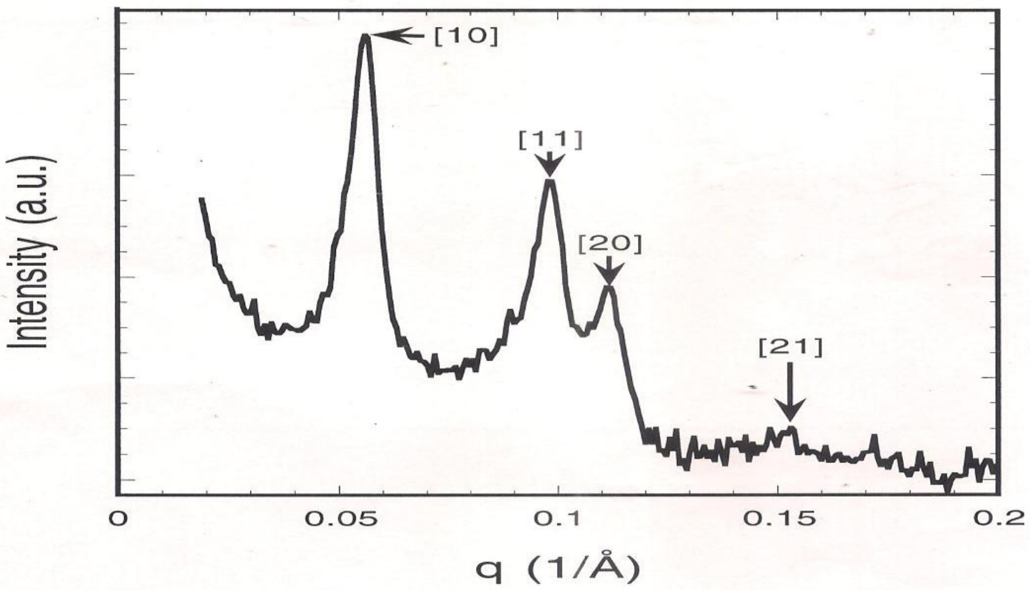


Figure 4.3 A SAXS diffraction pattern of samples in the H_1 region for the P104/D_2O/Benzyl Alcohol system at 25 ^{0}C.

4.2.1.3 Lamellar Liquid Crystalline Phase (Lα)

In a lamellar phase, samples have the simplest, one dimensional microstructure, consisting of lamellae (planar micelles). Macroscopically, samples in lamellae region are cloudy, optically birefringent and less stiff compared with samples in hexagonal phases (Svensson *et al.*, 1998). Lamellar phase is formed in the binary water – copolymer axis at copolymer range of between 85 wt% to 52 wt% and swells up to 20 wt% of benzyl alcohol. Therefore, the lamellar phase contains quite a lot of water (80 wt% and above). One-dimensional lamellar structure was established by SAXS measurements that gave different patterns with second and even third order Bragg peaks. Typical scattering diffraction patterns of samples belonging to the Lamellae (Lα) domains are presented in Figure 4.4. The scattering profiles of the samples showing diffraction peaks in the relative positions 1:2:3--- confirm the lamellar structure.

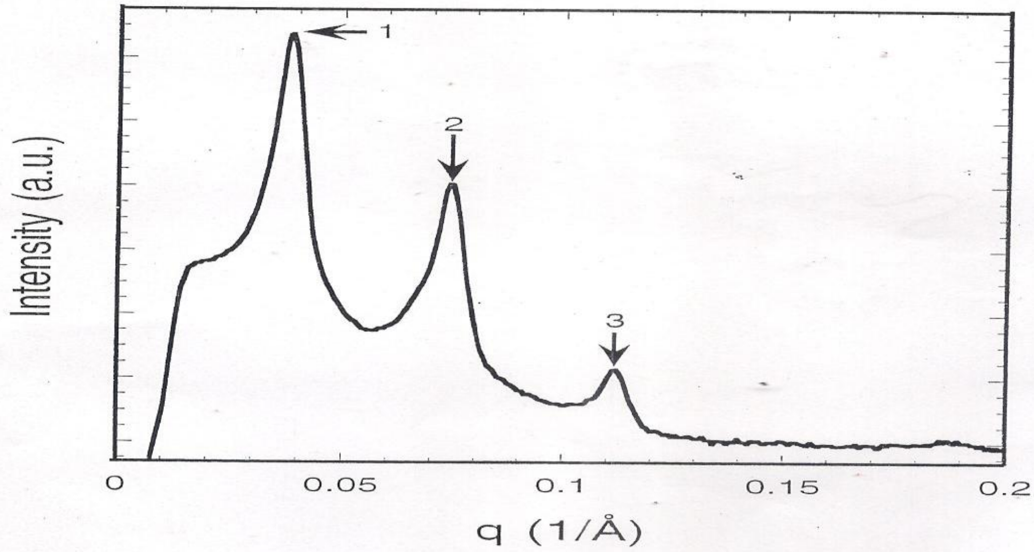


Figure 4.4 A SAXS diffraction pattern of samples in the Lα region for P104/D_2O/benzyl alcohol system at 25 ^{0}C.

4.2.1.4 Normal Micellar (L_1) and Reverse Micellar (L_2) Isotropic Solutions in P104 system

In addition to the four liquid crystalline microstructures, two isotropic solution regions, L_1 and L_2 are present in water-rich and water-lean sides of the ternary phase diagram respectively. In the L_1 phase, micelles can form without oil, while in L_2 phase; micelle formation requires a small amount of water. An isotropic water-rich region is found along a copolymer-water axis, up to 21 wt% of copolymer and can solubilize about 9 wt% of benzyl alcohol. Reverse micellar (L_2) phase is more extensive, extending up to 75 wt% copolymer along the copolymer-oil axis. The copolymer has a 60 wt% hydrophobic section and therefore it is very soluble in benzyl alcohol. Reverse micelles can solubilize a maximum of 17 wt% water before phase separation occurs. L_1 and L_2 micellar solution phases are isotropic optically transparent but they progressively become more viscous as the quantity of copolymer increases (Kipkemboi *et al*., 2003).

4.2.2 Phase Behavior and Structure of L62/D_2O/Benzyl Alcohol Ternary System

This copolymer is very hydrophobic and asymmetric in the PEO-PPO composition since it contains about 21 wt% PEO and 79 wt% PPO. Because of the low PEO block molecular weight, the PEO does not crystallize at low temperatures and therefore the copolymer is disordered at ambient temperatures. The isothermal phase diagram of the L62/D_2O/Benzyl alcohol ternary system at 25 ^{0}C is presented in Figure 4.5. Solid lines indicate boundaries of one-phase regions. Samples whose compositions fall outside the one-phase regions are dispersions of two or three phases. There was only lyotropic liquid crystalline phase formed by this ternary system.

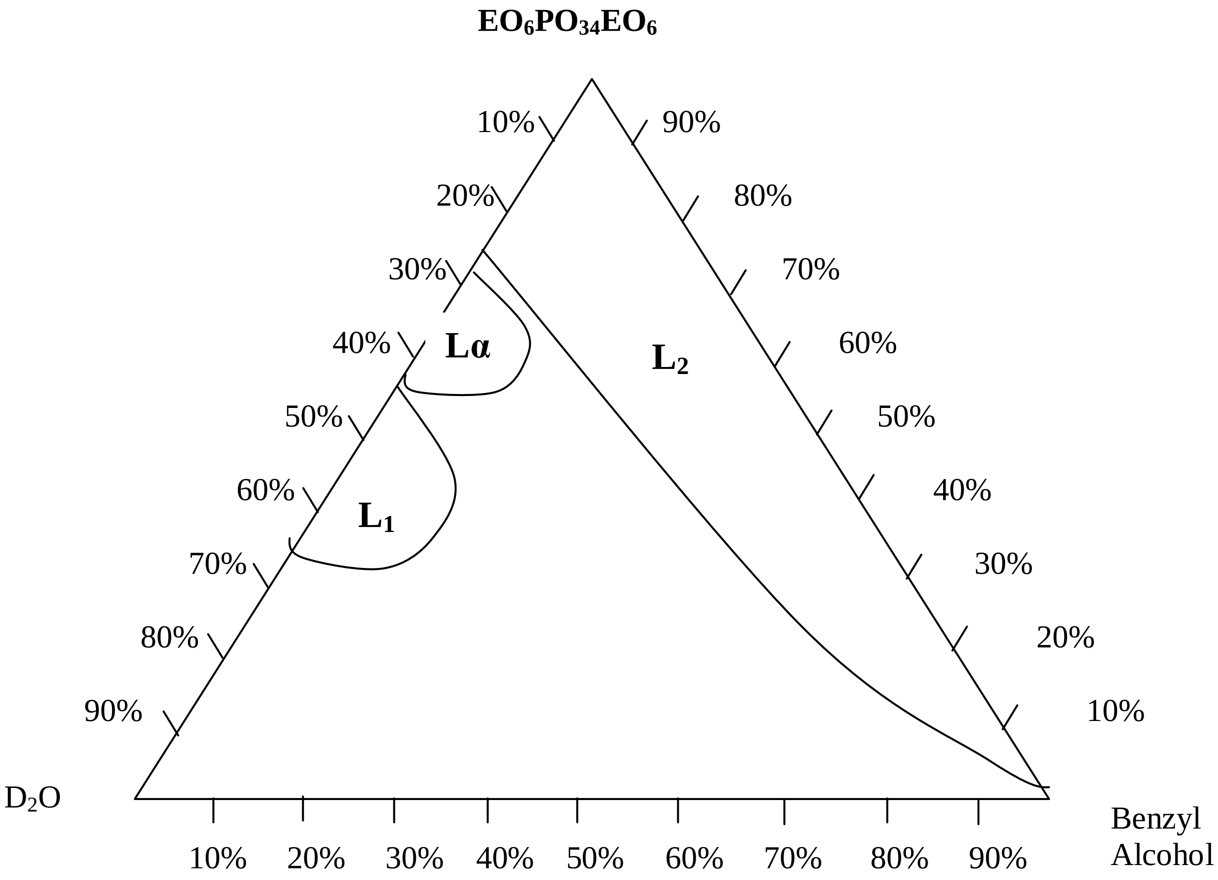


Figure 4.5 Isothermal phase diagram of the L62/D_2O/Benzyl alcohol ternary system at 25 ^{0}C.

The homogeneous one-phase samples observed, when starting on the water axis and progressing clockwise over to the oil corner are the following: normal micellar solution phase (L_1), lamellar phase (Lα) and reverse micellar solution phase (L_2). The copolymer was found to be completely soluble in benzyl alcohol.

4.2.2.1 Lamellar Liquid Crystalline Phase (Lα)

The lamellar (Lα) phase was formed in the binary water-copolymer axis at copolymer concentration greater than 36 wt% and continued up to 50 wt% copolymer. The one-dimensional lamellar structure was established by SAXS measurements that gave different patterns with second and third order Bragg peaks. Relative positions of the peaks follow the expected sequence for a lamellar structure 1:2:3. Figure 4.6 presents a typical SAXS diffraction pattern from lamellar phase that was obtained in this ternary system.

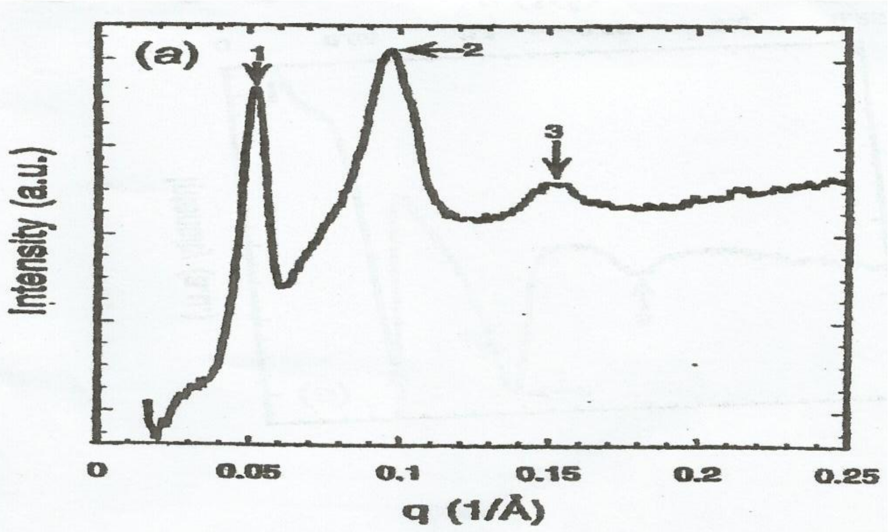


Figure 4. 6 Representative SAXS diffraction pattern of samples in the Lα phase for the L62/D_2O/benzyl alcohol ternary system at 25 ^{0}C.

4.2.2.2 Normal Micellar (L_1) and Reverse Micellar (L_2) Isotropic Solutions in L62 system

In addition to the lamellar liquid crystalline microstructure (Lα), two isotropic solution regions, L_1 and L_2 were formed in the water-rich corner and the water-lean side of the ternary phase diagram respectively. Similar to previous ternary phase diagram, in the L_1 phase, micelles can form without the presence of the oil, while in the L_2 phase micelles can form with a small amount of water. An isotropic water-rich region is found along a copolymer-water axis, up to 78 wt% of L62 copolymer from 51 wt% and can solubilize about 14 wt% of benzyl alcohol. The reverse micellar (L_2) phase is more extensive and it extends through a whole range of binary oil-polymer axis. It can solubilize a maximum of 22 wt% water before phase separation occurs. The L_1 and L_2 micellar solution phases are isotropic, optically transparent and fluid but they progressively become more viscous as the copolymer amount increases.

4.2.3 Discussion on phase behaviour

The isothermal phase diagrams of P104-water-benzyl alcohol and L62-water-benzyl-alcohol ternary systems are presented in Figures 4.1 and 4.5 respectively. The two ternary systems exhibited very different phase behaviors. The two block copolymers are asymmetrical in PEO-PPO blocks but L62 is more asymmetrical with 79 wt% PPO as compared to P104 with 60 wt% PPO. This difference in PEO-PPO compositions led to the P104-water-benzyl alcohol ternary system producing four lyotropic liquid crystals while L62-water-benzyl alcohol ternary system produced only lyotropic liquid crystalline phase.

P104 block copolymer is fairly symmetric and it was able to produce an almost symmetric phase behavior with respect to interchangeable of water in oil volume fractions. The ternary system of P104-water-benzyl alcohol, however, gave one reverse lyotropic liquid crystalline phase and two normal lyotropic phases besides the lamellar phase which normally appears almost at the central region of the two selective solvents. The ternary system P104-water-benzyl alcohol produced a lower number of lyotropic liquid crystalline phases and not as symmetrical as in those produced by P104-water-p-xylene (Figure 2.4). Therefore, *p*-xylene, a selective solvent for PPO block in the polymer produces a higher number of lyotropic liquid crystalline phases than benzyl alcohol.

L62-water-benzyl alcohol ternary system was only able to produce one lyotropic liquid crystalline phase, the lamellar phase, and could not give either normal or reverse phases. This ternary system containing a block copolymer that is highly asymmetric with a PPO molecular weight percentage of 79 wt% was expected to give phase behavior almost similar to that of $EO_4PO_{59}EO_4$-water-*p*-xylene ternary system where reverse phases are favoured (Kipkemboi *et al*., 2003). The results obtained from the ternary system L62-water-benzyl alcohol indicate that benzyl alcohol is not a good PPO selective solvent with respect to formation of lyotropic liquid crystalline phases as compared to *P*-xylene solvent.

4.3 Clouding Behavior of Nonionic Surfactant Solutions

One characteristic feature of nonionic surfactant solutions is their instant separation upon heating into two phases. The balance between hydrophilic/hydrophobic interactions is the most likely cause that determines the temperature at which this phase separation occurs. Nonionic surfactants change from water-soluble to oil soluble with increasing temperature. The temperature at which this phase separation occurs is known as cloud point (CP). Cloud point is said to be the temperature above which surfactant phases separate and precipitate from solution (Gu and Galera, 1995).

4.3.1 CP of Aqueous Solutions of L62, P104 and Brij-78

Cloud points of solutions of L62, P104 and Brij-78 were measured at different surfactant concentrations and recorded in Appendices 1 and **2**. The cloud points of these aqueous solutions were used to plot graphs of CP versus surfactant in molL^{-1} and presented in Figures 4.7 and 4.8.

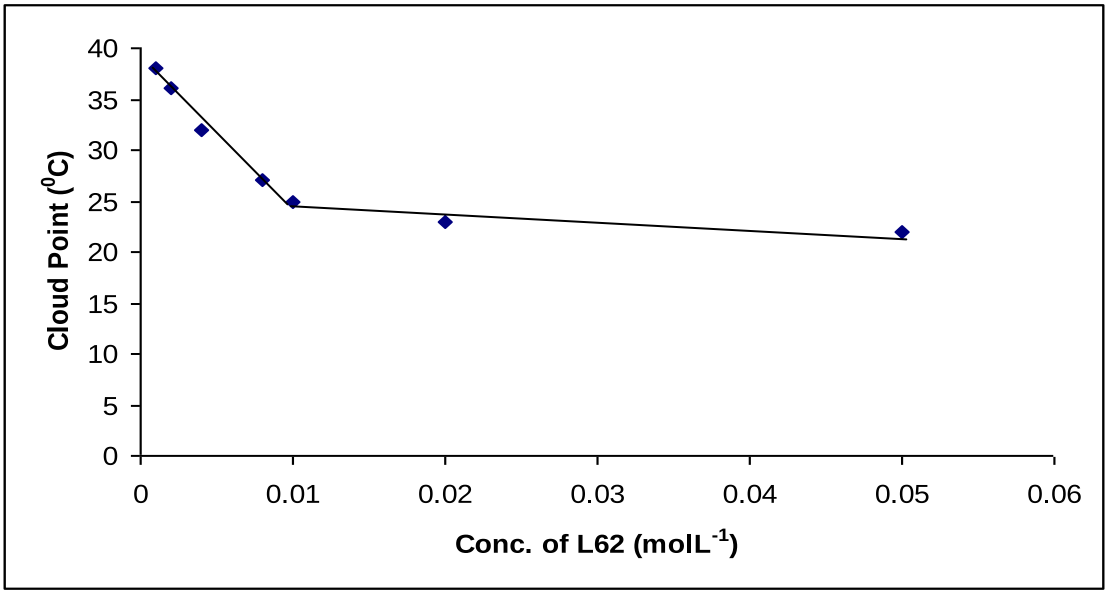


Figure 4.7 Cloud point versus concentration of L62 (molL^{-1})

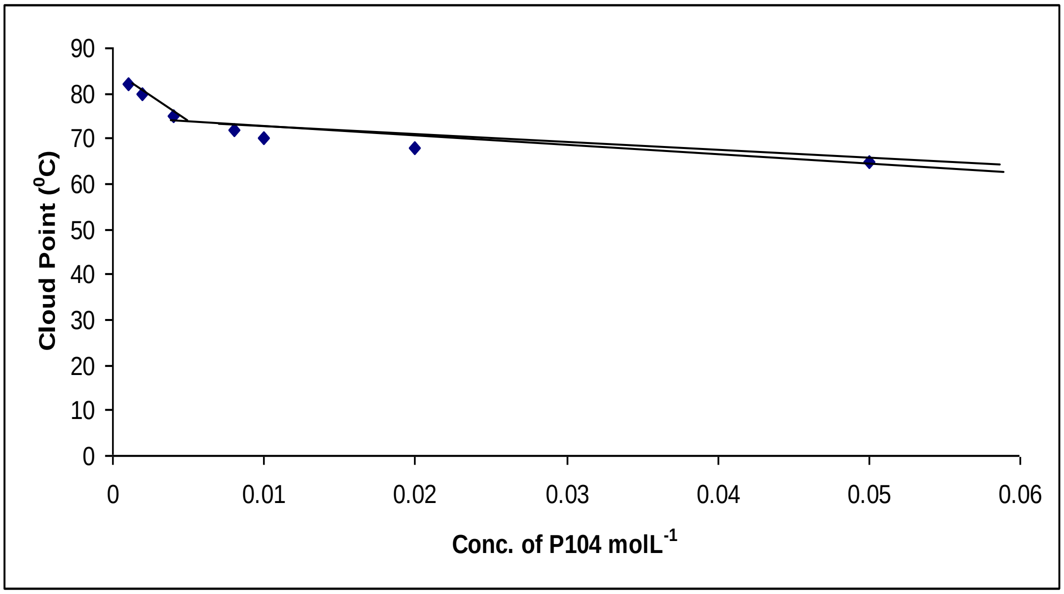


Figure 4.8 Cloud point versus concentration of P104 (molL^{-1}).

CP of block copolymers L62 and P104 was observed to be dependent on the polymer concentration decreasing slowly with increasing polymer concentration as shown in Figures 4.7 and 4.8. The general decrease in CP is in agreement with earlier studies (Soumen and Moulik, 1999) who observed that the CP of a nonionic surfactant is a function of its concentration and it decreases with increase of the surfactant concentration. The CP reduced from 38 ^{0}C at a surfactant concentration of 0.001 molL^{-1} to 25 ^{0}C at 0.01 molL^{-1} in the case of L62 and from 82 ^{0}C at 0.001 molL^{-1} to 75 ^{0}C at a concentration of 0.004 molL^{-1} in the case of P104 solutions steeply in each case before becoming less steep. Less steep decreasing curves are observed between concentrations of 0.01 molL^{-1} to 0.05 molL^{-1} and 0.004 molL^{-1} to 0.05 molL^{-1} for L62 and P10 solution4s respectively. The critical micelle concentrations (CMC) were thus observed to occur at 0.01molL^{-1} of L62 and 0.004 molL^{-1} of P104 respectively.

4.3.2 Effect of Inorganic Salts (NaCl, Na_2SO_4 and $AlCl_3$) on CP of L62, P104 and Brij-78 Aqueous Solutions

Inorganic salts, NaCl, Na_2SO_4 and $AlCl_3$ were added to the aqueous solutions of the nonionic surfactants L62, P104 and Brij-78 and the cloud point of their solutions determined. Cloud points of the solutions are presented in appendices 4, 5 and 6. The cloud points recorded were used to plot graphs of CP versus salt additive concentration in $molL^{-1}$ and are presented in Figures 4.9-4.11.

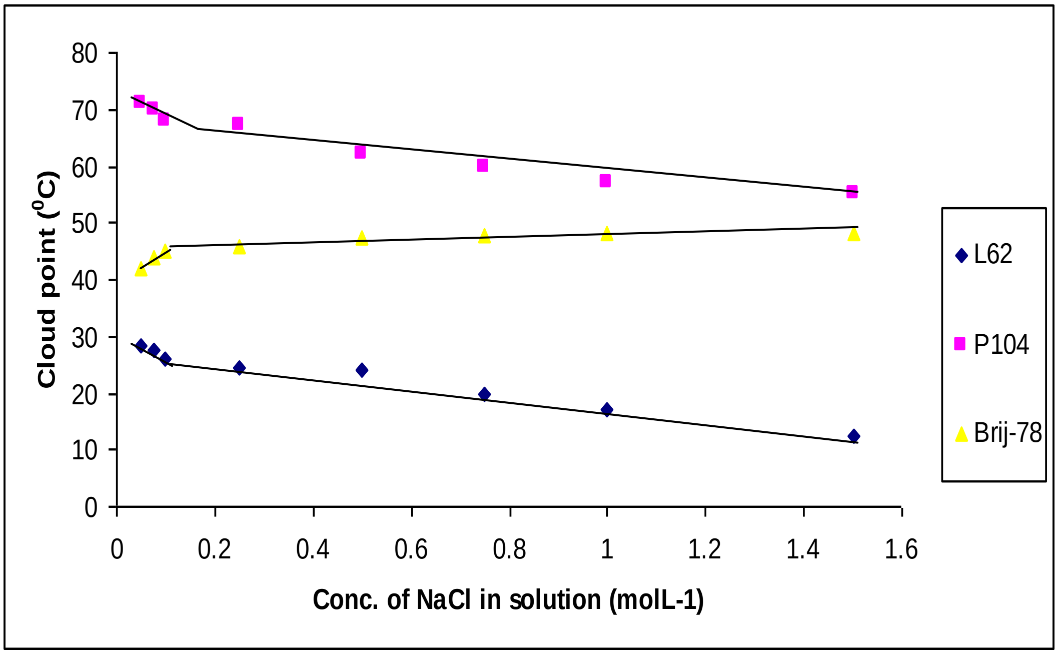


Figure 4.9 Effect of NaCl concentrations on cloud point of L62, P104 and Brij-78 (1 wt% of polymer).

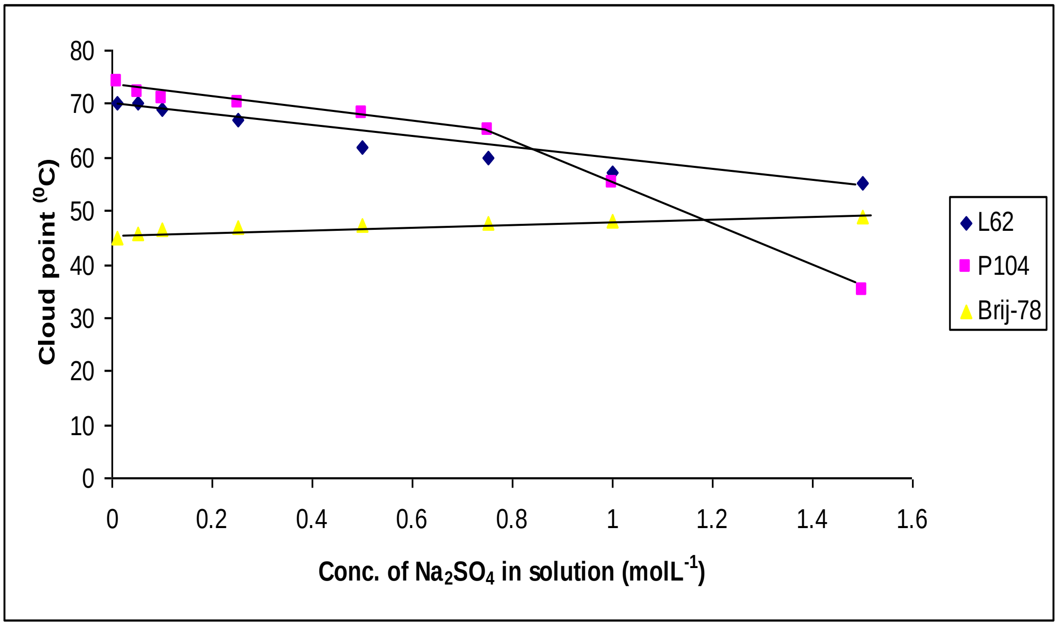


Figure 4.10 Effect of Na_2SO_4 concentrations on cloud point of L62, P104 and Brij-78 (1 wt% of polymer).

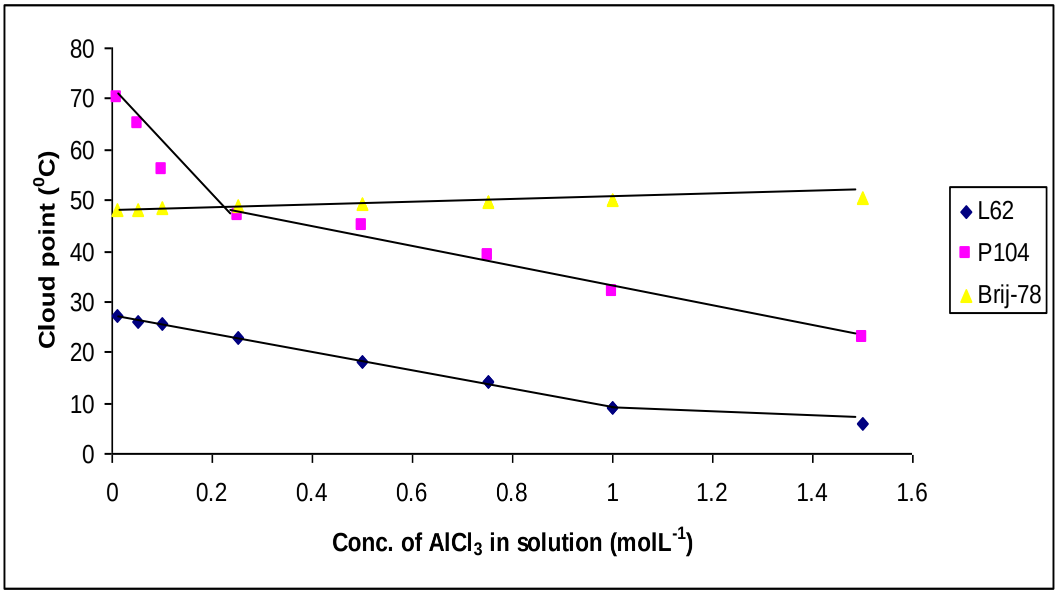


Figure 4.11 Effect of $AlCl_3$ concentrations on cloud point of L62, P104 and Brij-78 (1 wt% of polymer).

Variations of the cloud point for L62, P104 and Brij-78 polymer solutions as a function of the concentration of inorganic salts (NaCl, Na_2SO_4, and $AlCl_3$) are presented in Figures 4.9–4.11. There was a general decrease of CP for both L62 and P104 solutions with increase in salt concentration while in Brij-78 solution, a slight increase in CP was observed. From earlier studies (Travalloni- Louvisse and Gonzalez, 1998), inorganic salts cause a decrease in CP of nonionic surfactants, therefore these results agree well with those that have been observed previously except those of Brij-78 solutions.

All three salts produced a slight increase in the CP of Brij-78 solutions and NaCl was observed to have a bigger effect as compared to the other two. $AlCl_3$ gave the highest CP depression in both L62 (27 ^{0}C and 8 ^{0}C) and P104 (70 ^{0}C to 21 ^{0}C) while NaCl produced a lower depression effect in L62 (28.5 ^{0}C to 12.5 ^{0}C) and in P104 (71 ^{0}C to 55 ^{0}C). Na_2SO_4 had a higher depression effect than NaCl in the two surfactants but lower than $AlCl_3$.

Cloud point of Brij-78 solutions containing $AlCl_3$ increased slightly from 48 ^{0}C to 50.5 ^{0}C for a salt concentration of 0.05 $molL^{-1}$ to 1.5 $molL^{-1}$ while Na_2SO_4 raised it from 45 ^{0}C to 49 ^{0}C in the same salt concentration range and NaCl raised it from 42 ^{0}C to 48.2 ^{0}C respectively. The raising of CP by inorganic salt additives in Brij-78 solution contradicted earlier results (Travalloni- Louvisse and Gonzalez, 1998)..

The CMC for both $EO_6PO_{34}EO_6$ and Brij-78 solutions in NaCl was at a salt concentration of 0.1 $molL^{-1}$ while $EO_{27}PO_{61}EO_{27}$ has its CMC at a salt concentration of 0.075 $molL^{-1}$. P104 in Na_2SO_4 had its CMC at 0.75 $molL^{-1}$. The solutions of L62 and Bj-78 gave no CMC within the salt concentrations used since the curves of concentration of Na_2SO_4 against CP were straight throughout those concentrations.

4 .3.3 Effect of Added Ionic Surfactant (SDS and CTAB) on CP of L62, P104 and Brij-78 Aqueous Solutions.

Variations of the cloud point for L62, P104 and Brij-78 polymer solutions as a function of the concentration of ionic surfactants (SDS and CTAB) are presented in Appendices 7 and 8**.** CP of all the three nonionic surfactants was raised by both SDS and CTAB to above 100^0C. This is in agreement with Scamehorn (1986) who stated that the CP of an aqueous and dilute nonionic surfactant solution increases upon addition of ionic surfactant. To explain this phenomenon, various suggestions have been given which include the formation of mixed micelles, solubilization or complex formation (Schott and Royce, 1984).

Incorporation of ionic surfactant into nonionic micelles introduces electrostatic repulsion between the micelles, thus hindering the coacervate phase formation hence raising CP. Very low concentration of ionic surfactant strongly increases solubility and thus also CP of nonionic surfactants. This is due to the formation of mixed micelles in the case of clouding surfactant, and to an association of the surfactant-to-polymer in the case of clouding polymer. This result in charged aggregates which are much more difficult to concentrate in one of the phases due to unfavourable electrostatic interactions arising from the entropy of the counter ion destruction (Scamehorn, 1986).

4.3.4 Effect of Added Non-ionic Surfactant (TX-114) on CP of P104 and Brij-78 Aqueous Solutions

The nonionic surfactant TX-114 was mixed with other nonionic surfactant solutions of P104 and Brij-78 and the CP of these solutions determined and the results recorded in Appendix 9. Change of concentration of TX-114 was plotted against CP of P104 and Brij-78 solutions and the graphs obtained are presented in Figures 4.12 and 4.13 respectively.

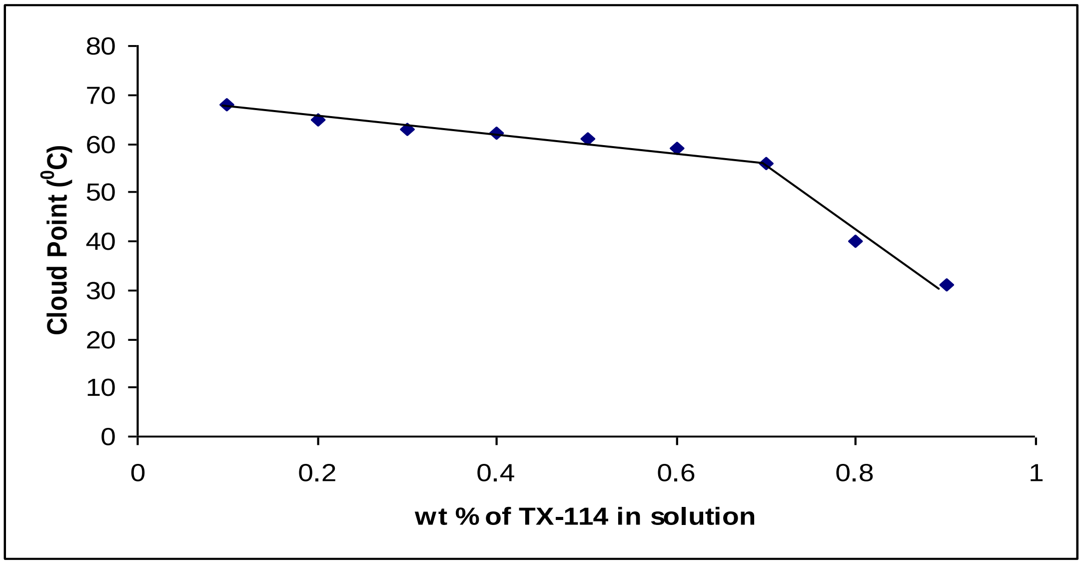


Figure 4.12 Cloud Point of P104 (1 wt %) versus wt % of TX-114.

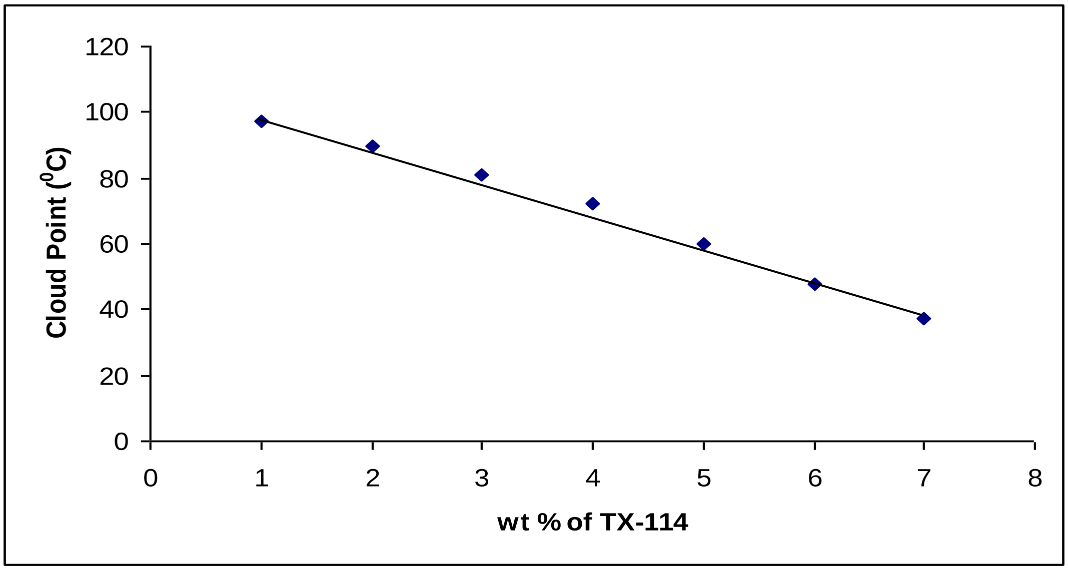


Figure 4.13 Cloud Point of Brij-78 (1 wt %) versus wt % of TX-114.

From Figures 4.12 and 4.13**,** it is observed that CP of both P104 and Brij-78 is lowered by adding the non-ionic surfactant (TX-114). This depression effect is seen to be more as the concentration of TX-114 increases. These results agree with earlier studies (Leszek, 1987) where use of non-ionic surfactant with a lower cloud point, depresses the CP of those non-ionic surfactant with very high CP.

CMC of P104 solution was observed to occur at ratio mixture of 0.7 wt % TX-114 to 1wt % of P104. The other two surfactant solutions did not show any CMC at the concentrations of TX-114 used.

4.4 Specific Conductivity of L62, P104 and Brij-78

Specific conductivity of aqueous solutions of these nonionic surfactants were determined when in pure solutions and with inorganic salt additives, ionic surfactant additives and one nonionic surfactant additive. The results obtained were used to plot graphs of surfactant concentrations against specific conductivity (Figures 4.14-4.16), concentration of inorganic salt additive against specific conductivity (Figures 4.17-4.19), concentration of ionic surfactant additive against specific conductivity (Figures 4.20-4.21) and wt% of nonionic surfactant against specific conductivity (Figure 4.22).

4.4.1 Specific Conductivity of Aqueous Solutions of L62, P104 and Brij-78.

Specific conductivity of aqueous solutions of L62, P104 and Brij-78 nonionic surfactants was measured at different surfactant concentrations at 25 ^{0}C. Specific conductivities of these aqueous solutions at different concentrations were recorded in Appendices 1, 2 and 3 respectively. The concentrations of the surfactants were plotted against the specific conductivity for each surfactant solution and are presented in Figures 4.14 - 4.16.

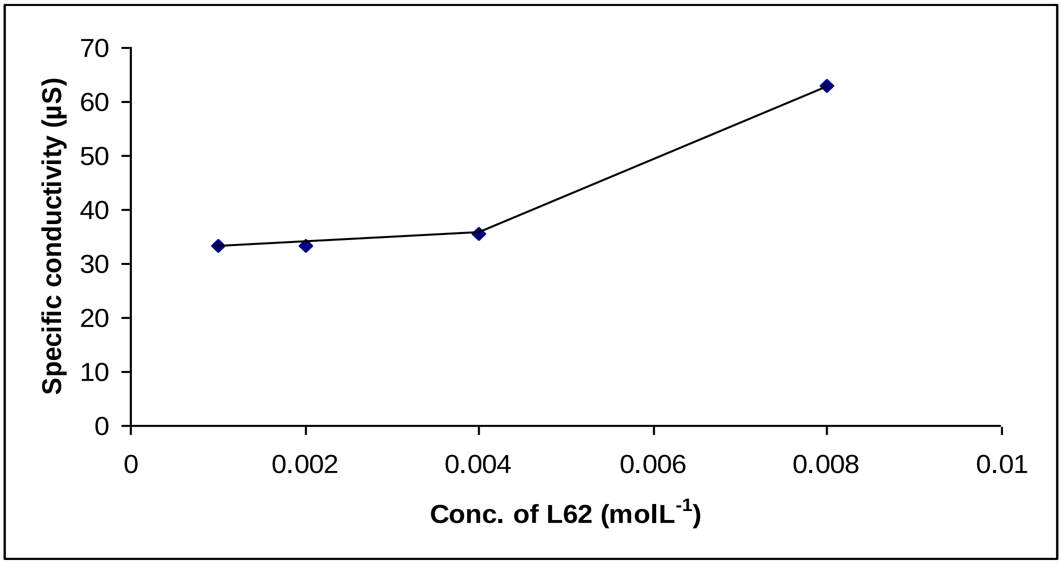


Figure 4.14 Specific Conductivity of aqueous solution of L62 versus surfactant concentration at 25 ^{0}C.

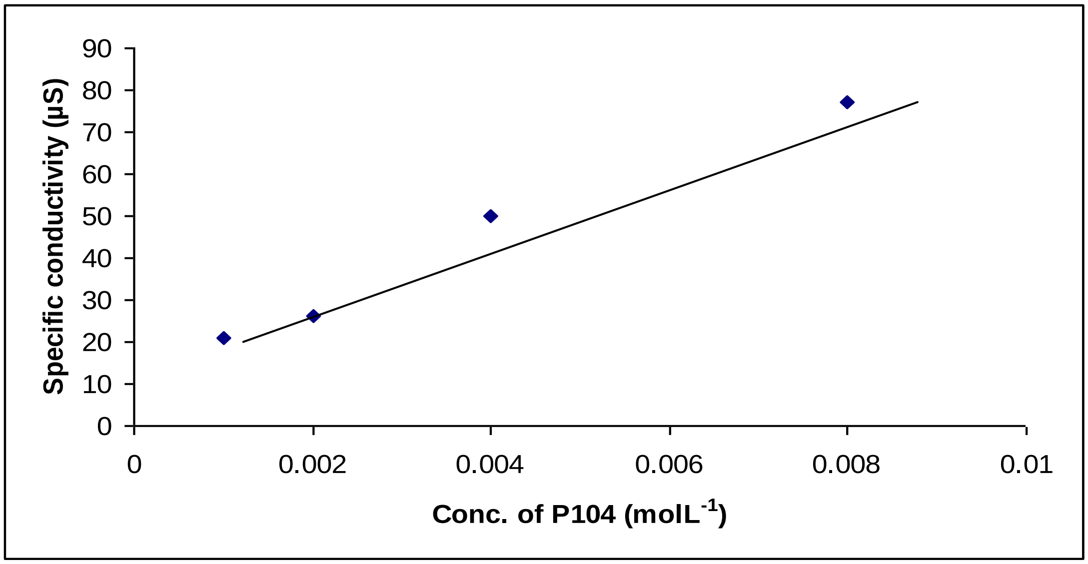


Figure 4.15 Specific Conductivity of aqueous solution of P104 versus surfactant concentration at 25 ^{0}C.

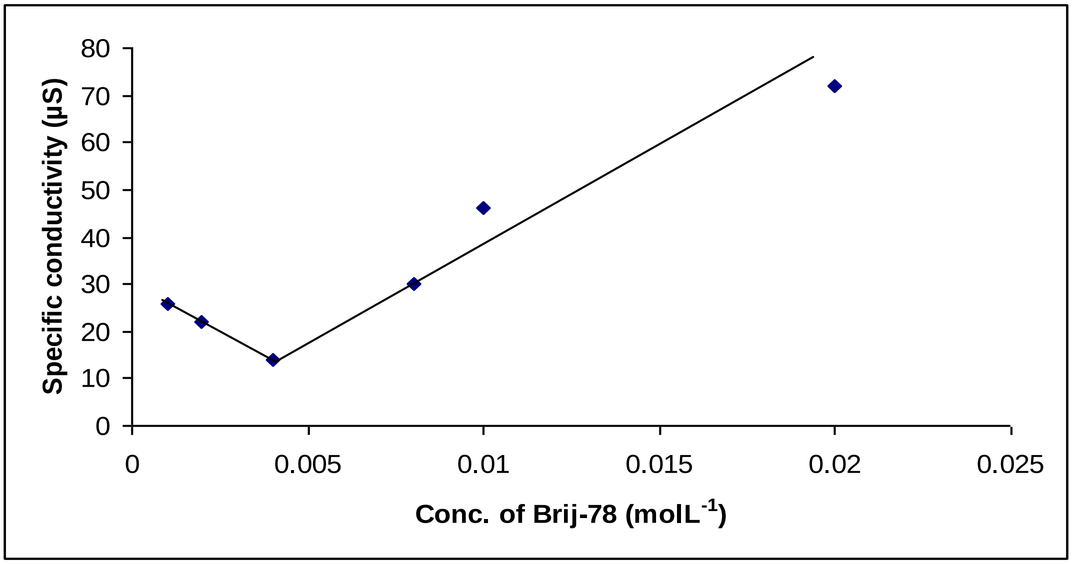


Figure 4.16 Specific Conductivity of aqueous solution of Brij-78 versus surfactant concentration at 25 ^{0}C.

Specific conductivity of aqueous solutions of all the three nonionic surfactants, L62, P104 and Brij-78 are presented in Figures 4.14 – 4.16. In all the cases, it was observed that specific conductivity increases with increase in surfactant concentration. For L62, specific conductivity rose slightly from 33.2 µS to 35.5 µS between surfactant concentrations of 0.001 $molL^{-1}$ and 0.004 $molL^{-1}$ and then rose a bit steeply from 35.5 µS (at a surfactant concentration of 0.004 $molL^{-1}$) to 63 µS (at a surfactant concentration of 0.008 $molL^{-1}$). For P104, specific conductivity rose from 21 µS to 77 µS at surfactant concentration of 0.001 $molL^{-1}$ to 0.008 $molL^{-1}$ and for Brij-78, specific conductivity dropped from 26 µS to 14 µS at a surfactant concentrations of 0.001 $molL^{-1}$ to 0.004 $molL^{-1}$ and then rose from 14 µS to 72 µS at a surfactant concentrations of 0.004 $molL^{-1}$ to 0.02 $molL^{-1}$

Both L62 and Brij-78 solutions gave a CMC at a surfactant concentration of 0.004 $molL^{-1}$ while the P104 solution did not show CMC within the concentrations used.

4.4.2 Effects of Inorganic Salts (NaCl, Na_2SO_4 and $AlCl_3$) on Specific Conductivity of L62, P104 and Brij-78

Inorganic salts, NaCl, Na_2SO_4 and $AlCl_3$ were added to the aqueous solutions of the nonionic surfactants L62, P104 and Brij-78 and the specific conductivity of their solutions determined. Specific conductivities of the solutions are presented in appendices 10 – 12. Variations of the specific conductivity for L62, P104 and Brij-78 polymer solutions as a function of the concentration of inorganic salts (NaCl, Na_2SO_4, and $AlCl_3$) are presented in Figures 4.17 – 4.19.

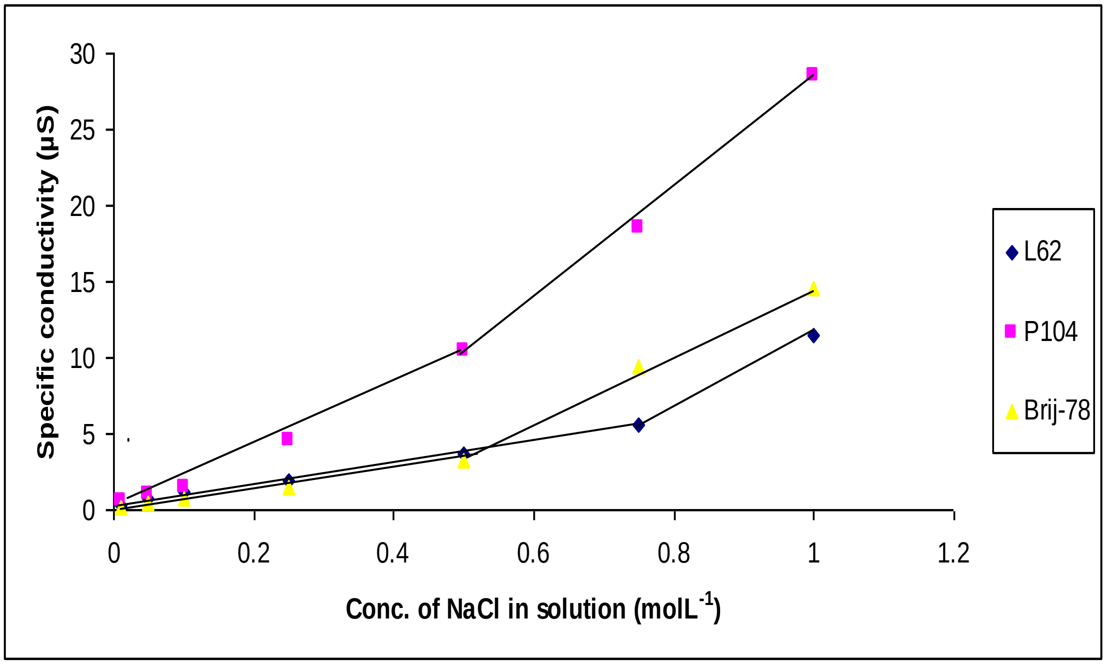


Figure 4.17 Specific Conductivity Versus concentration of NaCl in 1 wt % of L62, P104 and Brij-78

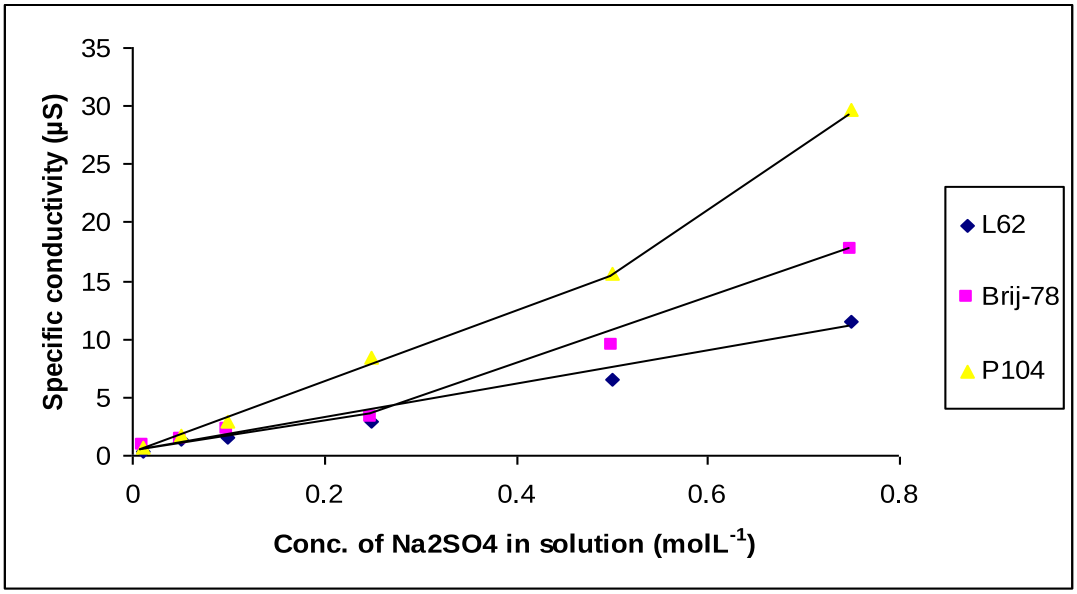


Figure 4.18 Specific Conductivity Versus concentration of Na_2SO_4 in 1 wt % of L62, p104 and Brij-78

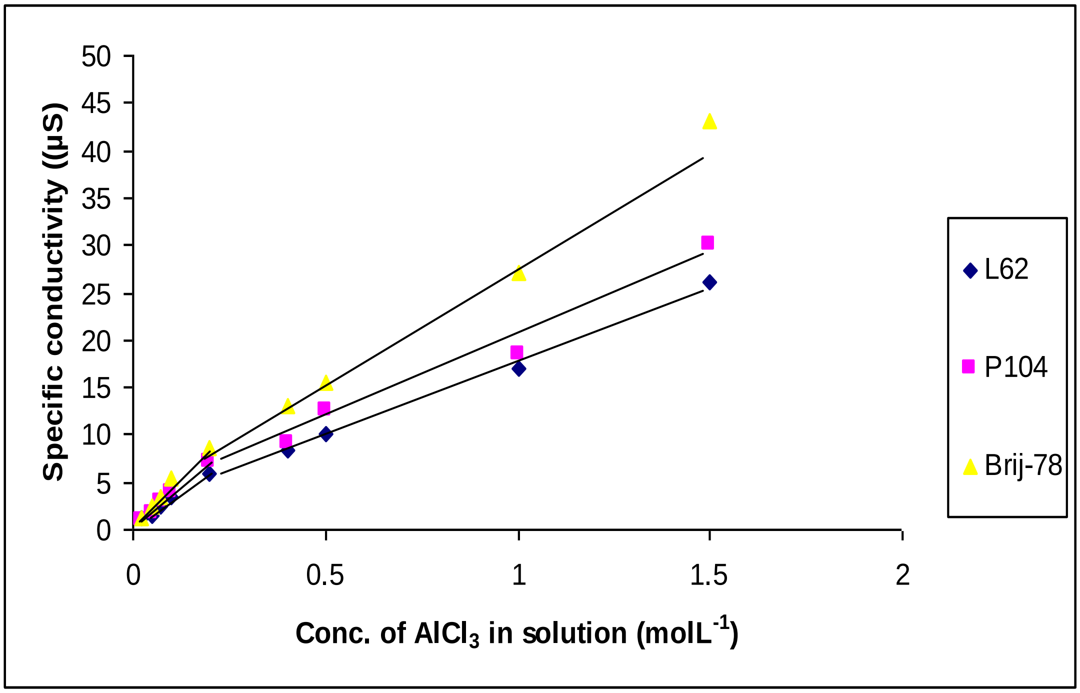


Figure 4.19 Specific Conductivity Versus concentration of AlCl$_3$ in 1 wt % of L62, P104 and Brij-78

There was a general increase of specific conductivity for all the solutions of the nonionic surfactants tested with increase in salt concentration. NaCl gave a slight increase in specific conductivity at the beginning with increase in salt concentration in all the three surfactants but it was steeper in P104. Specific conductivity of L62 increased from 0.24 µS (0.01 molL^{-1}) to 5.6 µS (0.75 molL^{-1}) less steeply and from 5.6 µS to 11.5 µS (1 molL^{-1}) more steeply. In P104, it increased less steeply from 0.6 µS (0.01 molL^{-1}) to 10.4 µS (0.5 molL^{-1}) but more steeply than in L62 before it became steeper from 10.4 µS (0.5 molL^{-1}) to 28.5 µS (0.75 molL^{-1}). The specific conductivity of Brij-78 in NaCl increased from 0.2 µS (0.01 molL^{-1}) to 3.2 µS (0.5 molL^{-1}) and then was raised more steeply to14.9 µS (0.75 molL^{-1}).

Na_2SO_4 produces the highest elevation effect in P104 with increase in salt concentration which became steeper between salt concentrations 0.5 molL^{-1} and 0.75 molL^{-1}. Specific conductivity increases from 0.81 µS to15.6 µS at salt concentrations of 0.01 molL^{-1} and 0.5 molL-1 before becoming steeper from 15.6 µS to 29.75 µS (0.75 molL^{-1} salt conc.). In Brij-78, it was raised from 0.81 µS to 2.35 µS at salt concentration of 0.01 molL^{-1} and 0.25 molL^{-1} less steeply and then became steeper from 2.35 µS to17.6 µS (0.75 molL^{-1}). In L62, specific conductivity was raised linearly and less steeply from 0.39 µS to 11.52 µS at salt concentrations of 0.01 molL^{-1} and 0.75 molL^{-1}. Specific conductivity raising effect was therefore highest in P104 followed by Brij-78 and was least in L62 solutions respectively.

$AlCl_3$ salt produced a steep increase in all three surfactant solutions with increase in salt concentration up to a salt concentration of 0.2 molL^{-1}. The curves for the three solutions then became slightly less steep and increased to 25 µS in L62, to 29.5 µS in P104 and 41.5 µS in Brij-78 solutions respectively when salt concentration was increased to1.5 molL^{-1}.

Values of CMCs for L62, P104 and Brij-78 solutions were observed at NaCl concentrations of 0.5 molL^{-1}, 0.75 molL^{-1} and 0. 5 molL^{-1} respectively. Solutions of the surfactants containing Na_2SO_4 did not show a CMC except P104 solution that gave a CMC at 0.5 molL^{-1}.

Values of CMCs for L62, P104 and Brij-78 solutions were observed at $AlCl_3$ concentrations of 0.2 $molL^{-1}$

4.4.3 Effect of Ionic Surfactants (SDS and CTAB) on Specific Conductivity of L62, P104 and Brij-78 Aqueous Solutions.

Specific conductivity versus concentration curves for nonionic surfactant additives SDS and CTAB containing L62, P104 and Brij-78 polymers are presented in Figures 4.20 and 4.21. The data is also summarized in Appendices 13 and 14.

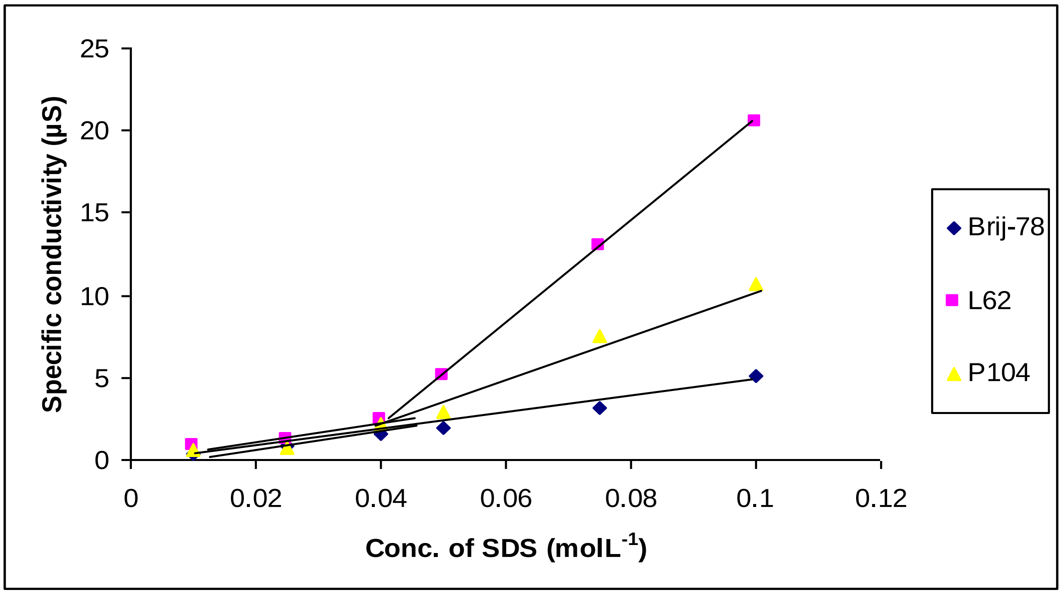


Figure 4.20 Effect of SDS on Specific Conductivity for aqueous solutions of L62, P104 and Brij-78.

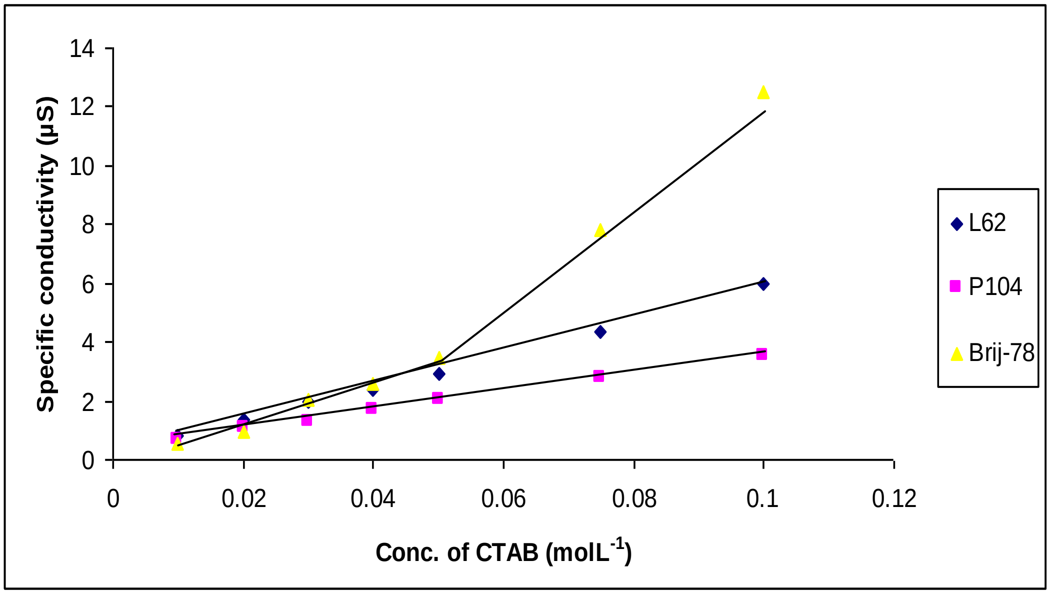


Figure 4.21 Effect of CTAB on Specific Conductivity for aqueous solutions of L62, P104 and Brij-78.

The two ionic surfactants used, one cationic (CTAB) and the other anionic (SDS) raised the specific conductivity in three nonionic solutions (L62, $P104_7$ and Brij-78). The anionic surfactant SDS produced the highest elevation effect in L62 while it gave the least elevation in Brij-78 solution. On the other hand cationic surfactant CTAB produced the highest elevation effect in Brij-78 solution while it produced the least elevation in P104 solution.

The CMCs of L62 and Brij-78 with SDS were observed at a surfactant additive concentration of 0.04 mol^{L-1}. In the case of CTAB cationic surfactant additive, CMC of Brij-78 solution was observed at 0.05 molL^{-1} of the cationic surfactant additive.

4.4.4 Effect of Non-ionic Surfactant (TX-114) on Specific Conductivity of L62, P104 and Brij-78 Aqueous Solutions

The effect of TX-114 on specific conductivity of L62, P104 and Brij-78 nonionic surfactant solutions was studied and recorded in Appendix 15. The concentration of TX-114 in the three nonionic surfactant solutions were plotted against specific conductivity and presented in Figure 4.22.

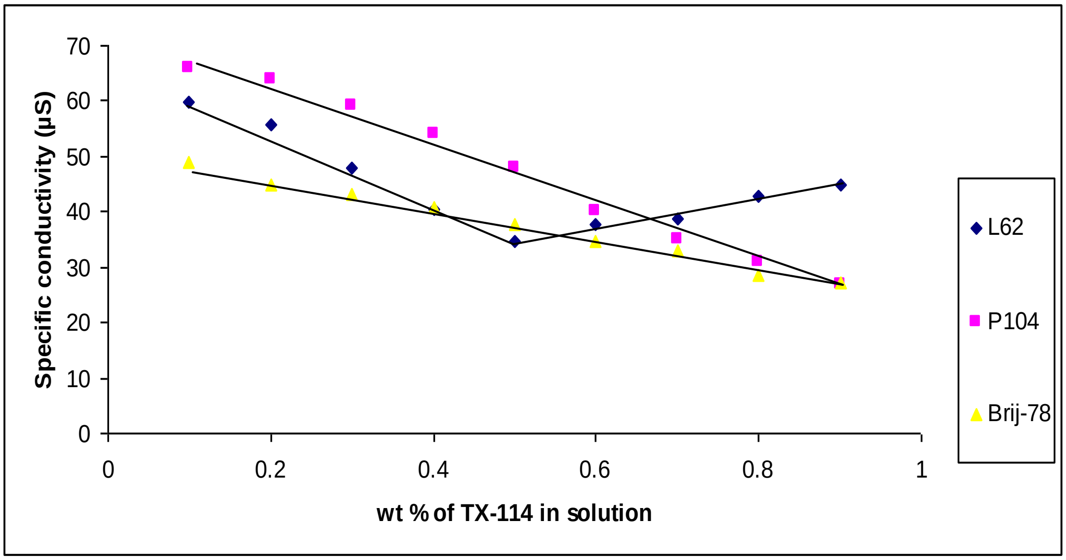


Figure 4.22 Effect of increasing wt % of TX-114 on Specific Conductivity (µ) of L62, P104 and Brij-78 solutions at a decreasing wt % of each polymer

TX-114 which is also a nonionic surfactant lowers the specific conductivity of all three surfactants. It is observed that depression of specific conductivity increases with increase in concentration of the nonionic surfactant additive (TX-114). In the case of L62 solution, specific conductivity decreased steadily from 60 ^{0}C at 0.1 wt% of surfactant additive 34.8 ^{0}C at 0.5 wt % of TX-114 in solution and it increases up to 0.9 wt% of TX-114. In both P104 and Brij-78 surfactants, the specific conductivity was depressed linearly and steadily but less steeply.

4.5 Measurement of Relative Viscosity

Relative viscosity of nonionic surfactants was studied in aqueous solutions and in solutions of the surfactants with additives such as inorganic salts, ionic and nonionic surfactants. Additives give an increase in relative viscosity of surfactants when they cause an increase in the size of the micelles formed (Prajapati and Patel, 2012). Relative viscosity of aqueous solutions of L62, P104 and Brij-78 nonionic surfactants were determined when in pure solutions and with inorganic salt additives, ionic surfactant additives and one nonionic surfactant additive. The results obtained were used to plot graphs of surfactant concentrations against relative viscosity (Figures 4.23-4.25), concentration of inorganic salt additive against relative viscosity (Figures 4.26-4.28), concentration of ionic surfactant additive against relative viscosity (Figures 4.29-4.30) and wt% of nonionic surfactant against relative viscosity (Figures 4.31-4.33). in cases where the curves showed a change in slope, CMC of the solutions were estimated

4.5.1 Relative Viscosity of Aqueous Solutions of L62, P104 and Brij-78

Figures 4.23-4.25 show the variation of relative viscosity as a function of the concentration of each of the polymers L62, P104 and Brij-78 in the absence of additives. The data is also summarized in appendices 16-18.

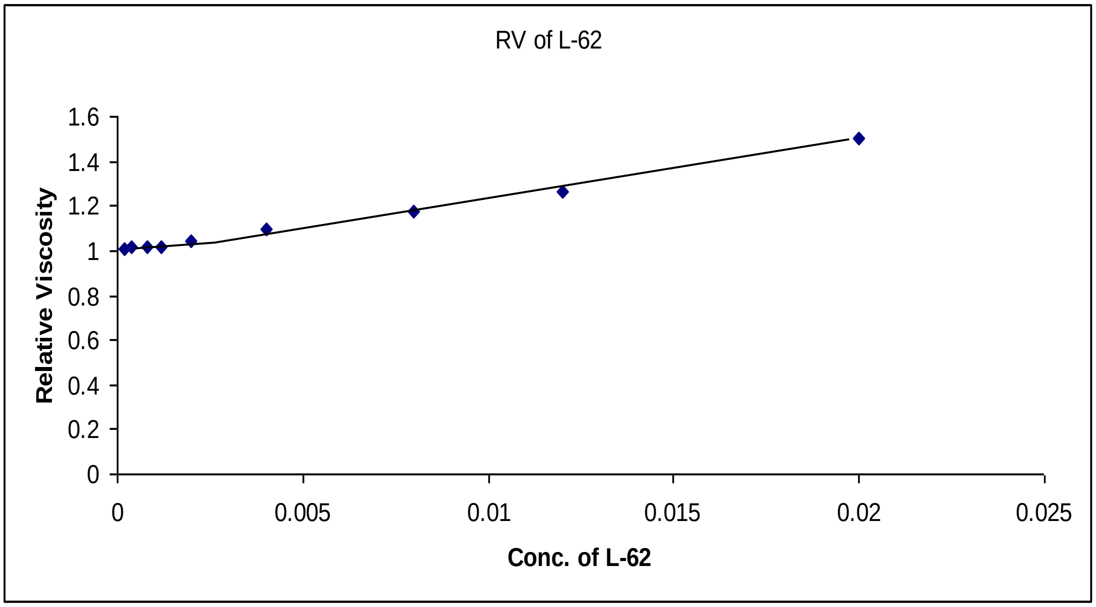


Figure 4.23 Relative Viscosity as a Function of L62 Concentration.

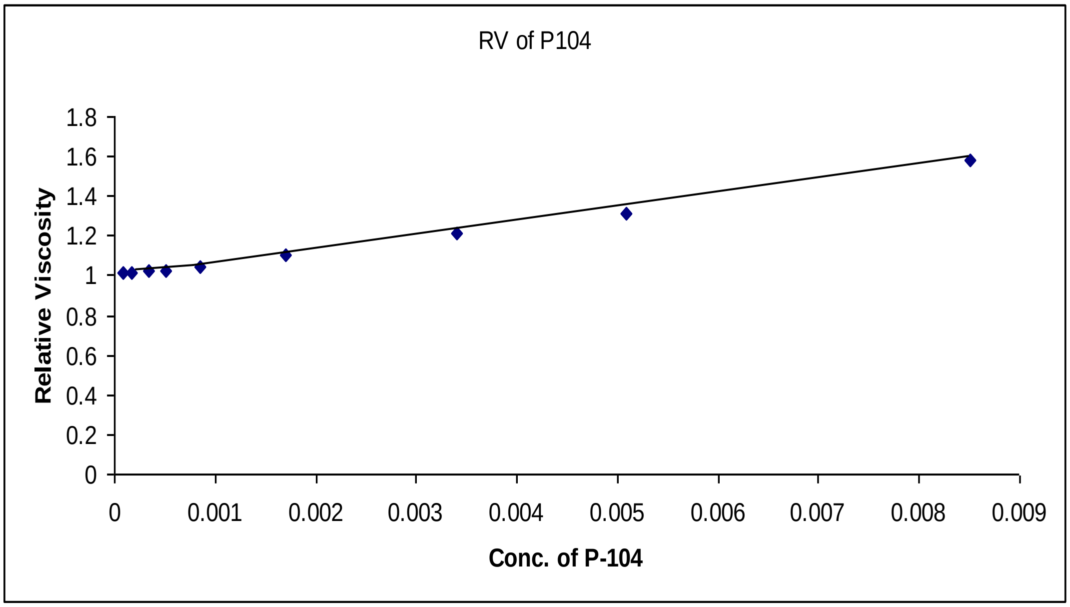


Figure 4.24 Relative Viscosity as a Function of P104 Concentration.

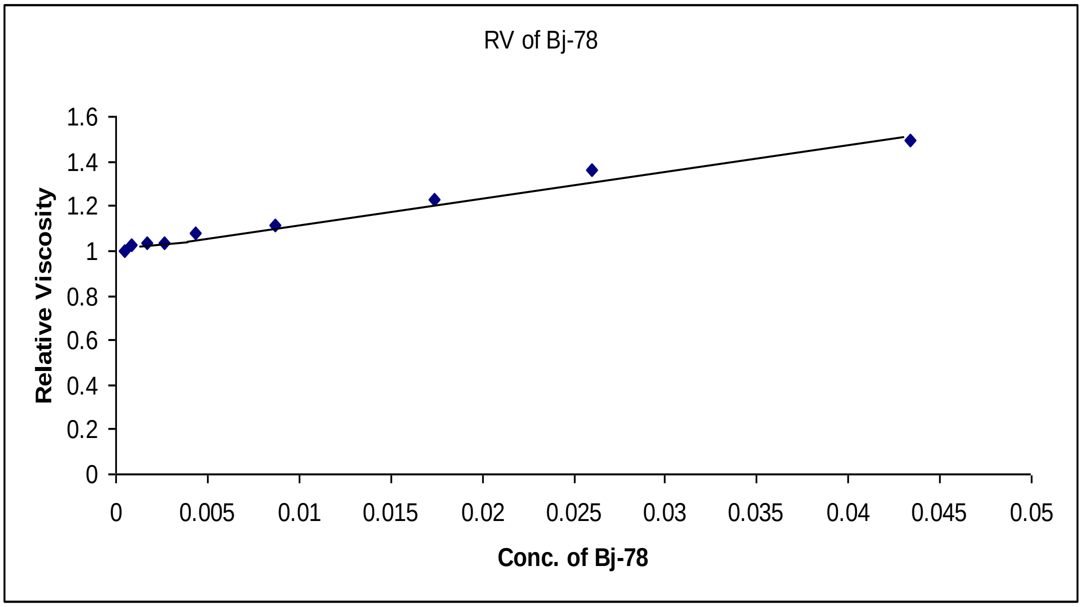


Figure 4.25 Relative Viscosity as a Function of Brij-78 Concentration.

For each aqueous polymer solution, the relative viscosity increases gradually and almost linearly with increase in surfactant concentration. This shows that as the concentration of the surfactant is increased, there are an increased number of surfactant molecules which lead to more tangling of these molecules. The result is an increase in viscosity since the molecules are not able to move more freely. All these surfactants are composed of long molecules (macromolecules) and because they are insoluble in water, they exist as long molecules in water which are not able to move freely. As the concentrations of the surfactants are increased, it becomes progressively more difficult for the solutions to flow hence increase in viscosity.

4.5.2 Effects of Inorganic Salts (NaCl, Na_2SO_4 and $AlCl_3$) on Relative Viscosity of L62, P104 and Brij-78

Effect of inorganic surfactants; NaCl, Na_2SO_4 and $AlCl_3$ on relative viscosity of solutions of L62, P104 and Brij-78 were measured and recorded in **Appendices 16-18**. The results obtained were used to plot graphs of relative viscosity as a function of surfactant concentration and presented in **Figures 4.26-4.28**.

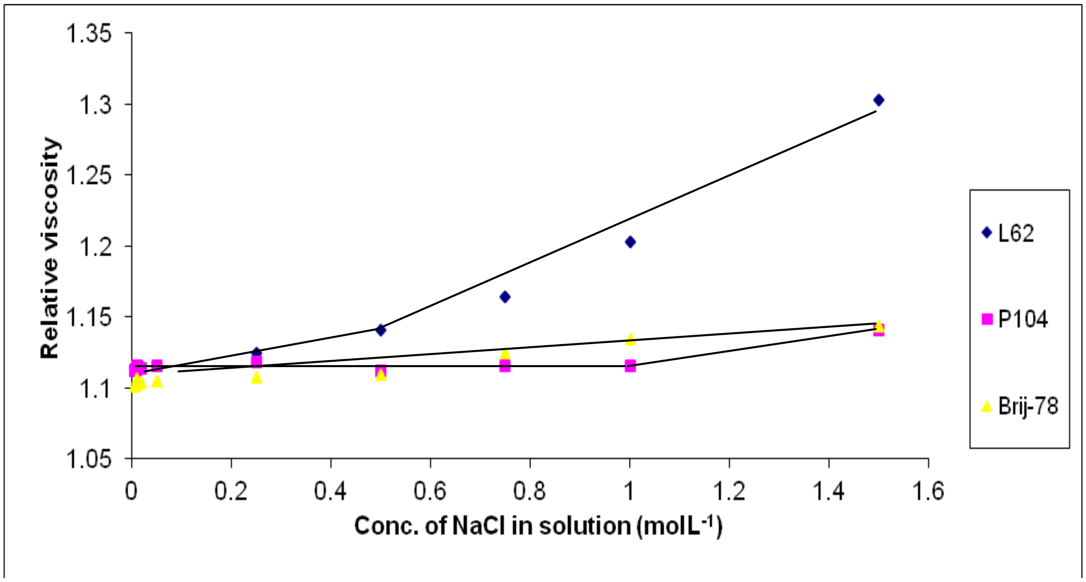


Figure 4.26 Relative Viscosity of a 1 wt% Solution of L62, P104 and Brij-78 as a function of NaCl concentration.

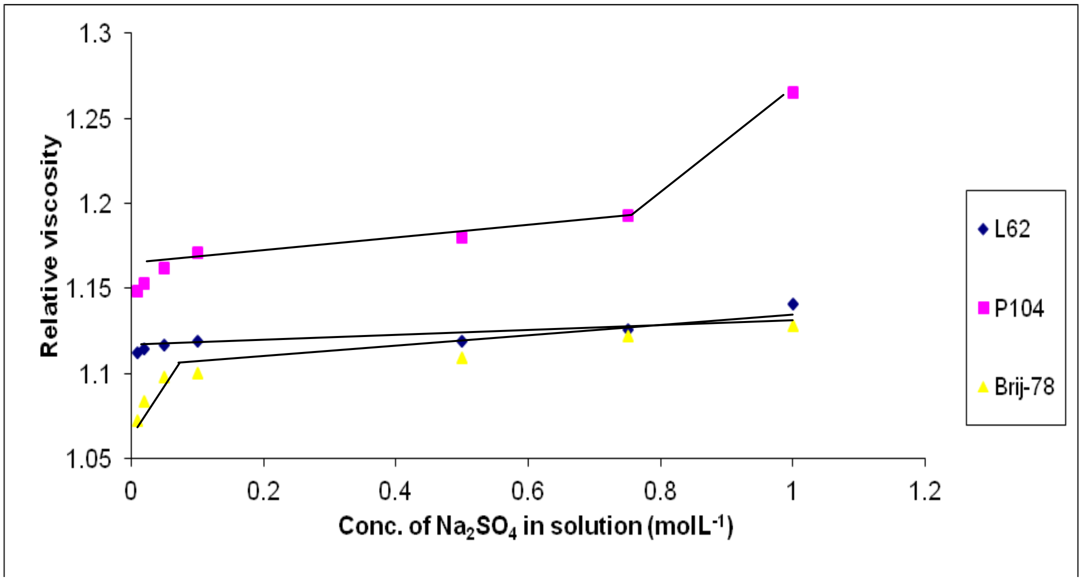


Figure 4.27 Relative Viscosity of a 1 wt % Solution of L62, P104 and Brij-78 as a function of Na_2SO_4 concentration.

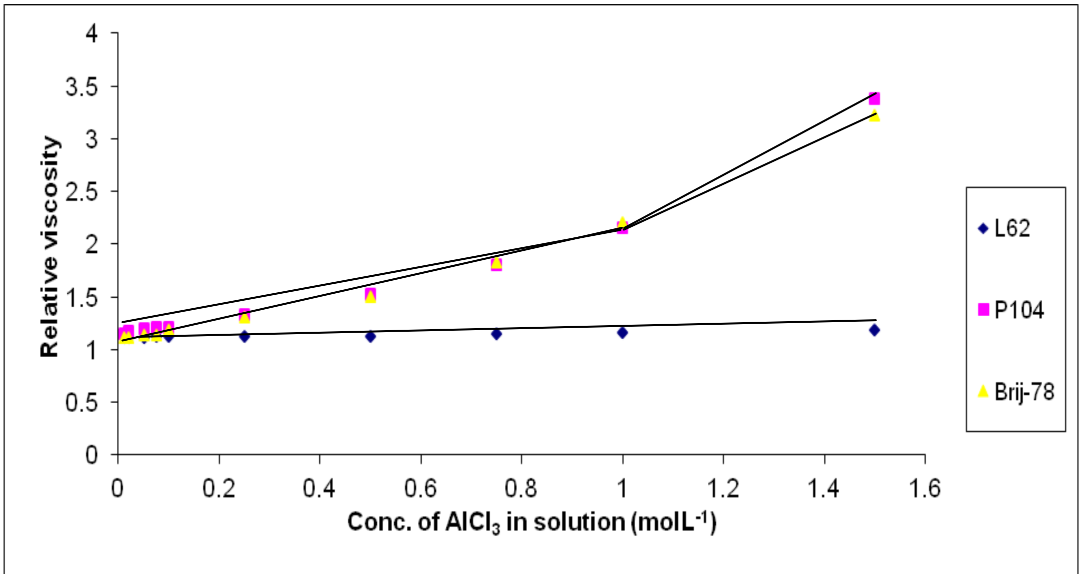


Figure 4.28 Relative Viscosity of a 1 wt% Solution of L62, P104 and Brij-78 as a function of $AlCl_3$ concentration.

Both NaCl and Na_2SO_4 inorganic salts give an increase in relative viscosity of the solutions of the three nonionic surfactants while $AlCl_3$ gives an elevation in both P104 and Brij-78 but has no effect on L62 nonionic surfactant solution. NaCl produces a very slight elevation of relative viscosity in P104 while Na_2SO_4 gave a slight increase of relative viscosity in Brij-78 solution.

Na_2SO_4 produces a significant increase in relative viscosity of P104 while in both L62 and a brij-78 solution, the increase is insignificant. Therefore, in P104 solution, Na_2SO_4 causes a remarkable increase in micelle size while in both L62 and brij-78 solutions, the micelle size increase are almost negligible. $AlCl_3$ does not have any effect in L62 solution but in both P104 and brij-78 solutions, a significant increase are observed indicating that in these two nonionic salts, $AlCl_3$ causes a remarkable increase in micelle size.

4.5.3 Effect of Ionic Surfactants (SDS and CTAB) on Relative Viscosity of L62, P104 and Brij-78 Aqueous Solutions.

Effect of ionic surfactants; SDS and CTAB on relative viscosity of solutions of L62, P104 and Brij-78 were measured and recorded in Appendices 19-20. The results obtained were used to plot graphs of relative viscosity as a function of surfactant concentration and presented in Figures 4.29-4.30.

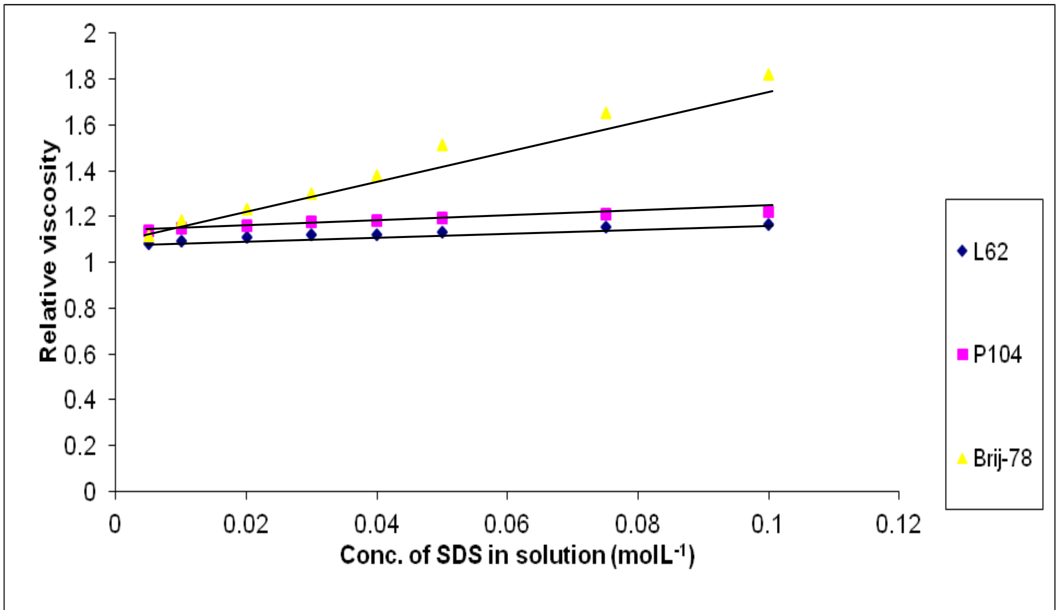


Figure 4.29 Relative Viscosity of a 1 wt % Solution of L62, P104 and Brij-78 versus SDS surfactant concentration.

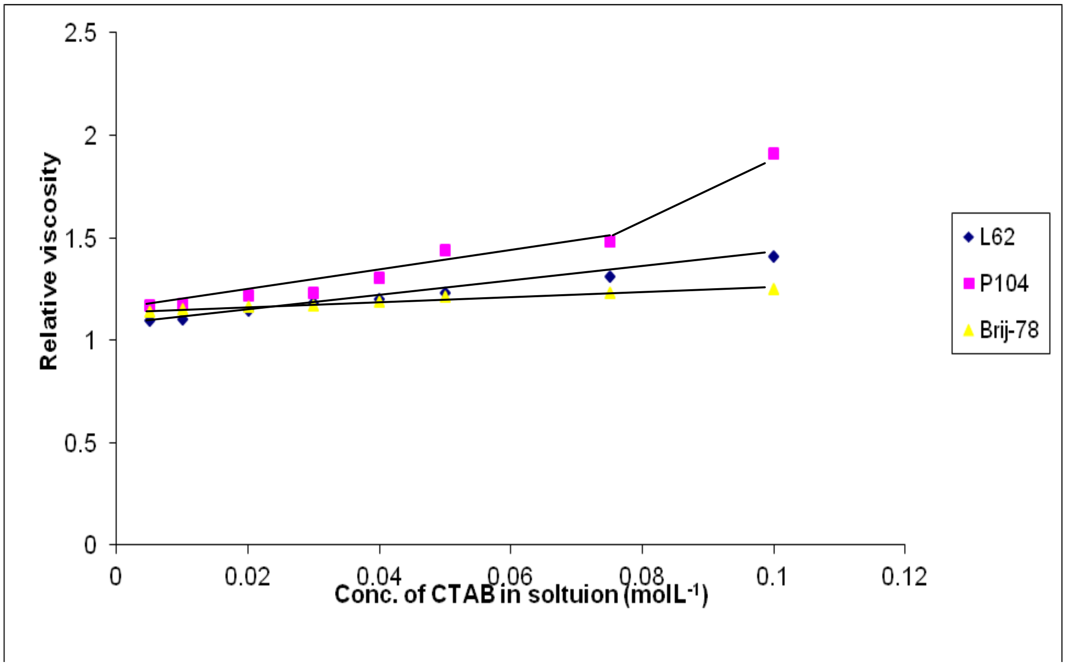


Figure 4.30 Relative Viscosity of a 1 wt% Solution of L62, P104 and Brij-78 versus CTAB concentration surfactant concentration.

The ionic surfactants SDS and CTAB gave a very slight increase in relative viscosity of the three nonionic surfactants except SDS in Brij-78 which was steeper and linear. Both L62 and P104 showed a very slight increase in relative viscosity with increase in the concentration of SDS surfactant additive. The surfactant solutions containing CTAB also gave a very slight increase in relative viscosity except P104 solution which was observed to have a slightly higher elevation.

4.5.4 Effect of Non-ionic Surfactant (TX-114) on Relative Viscosity of L62, P104 and Brij-78 Aqueous Solutions

Effect of a nonionic surfactant TX-114 on relative viscosity of solutions of L62, P104 and Brij-78 were measured and recorded in Appendix 21. The results obtained were used to plot a graph of relative viscosity as a function of surfactant concentration and presented in Figures 4.31-4.33.

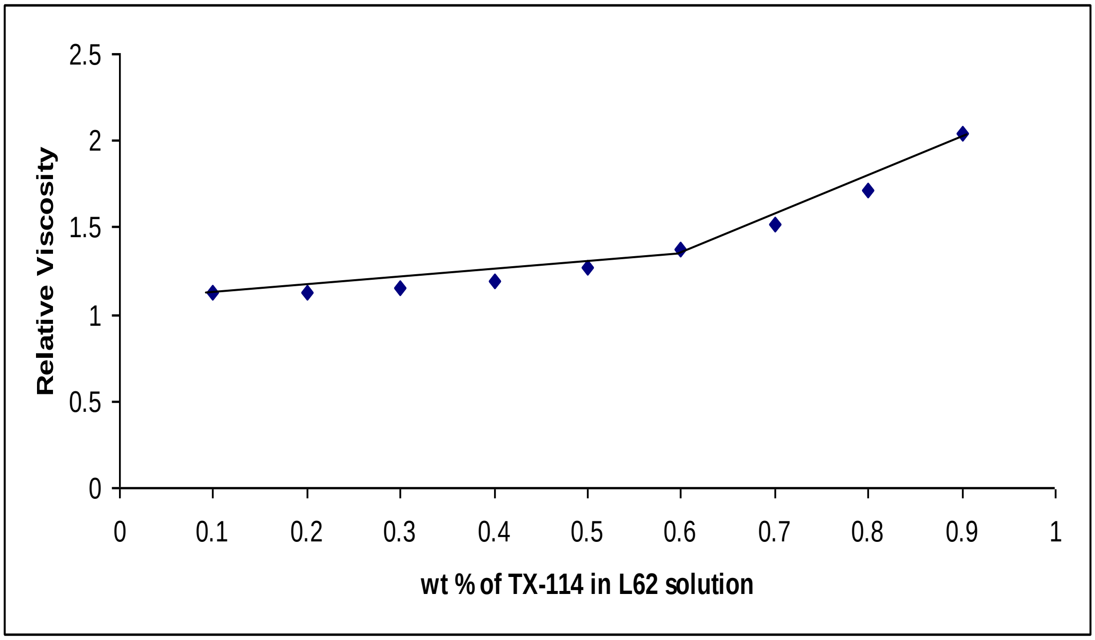


Figure 4.31 Effect of increasing wt % of TX-114 on Relative Viscosity of L62 solution at a decreasing wt % of the polymer.

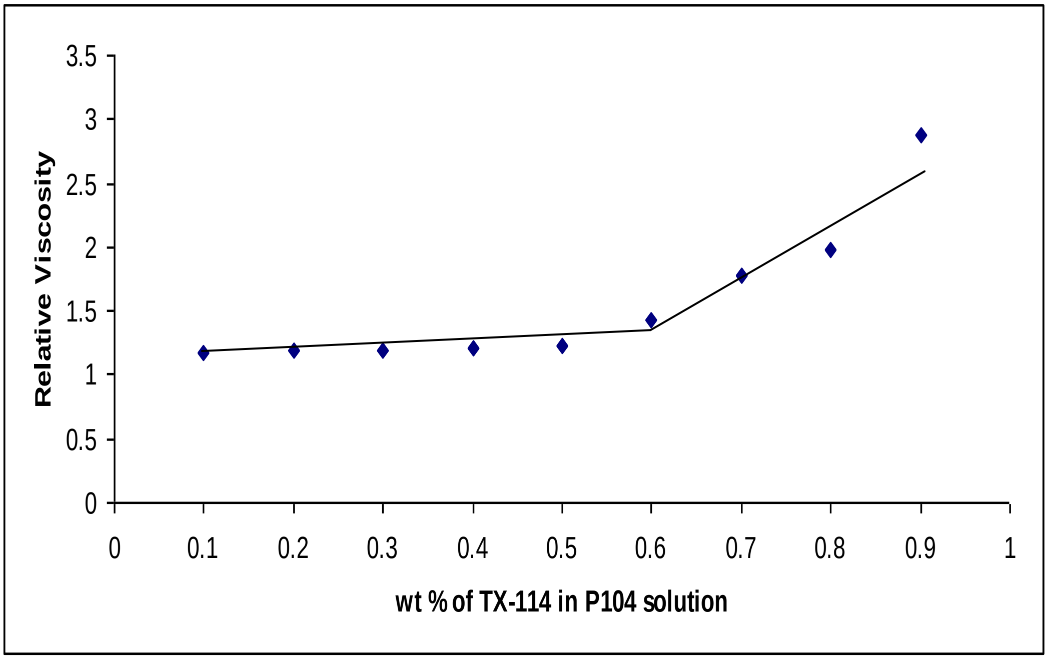


Figure 4.32 Effect of increasing wt % of TX-114 on Relative Viscosity of $O_{27}PO_{61}EO_{27}$ solution at a decreasing wt % of the polymer.

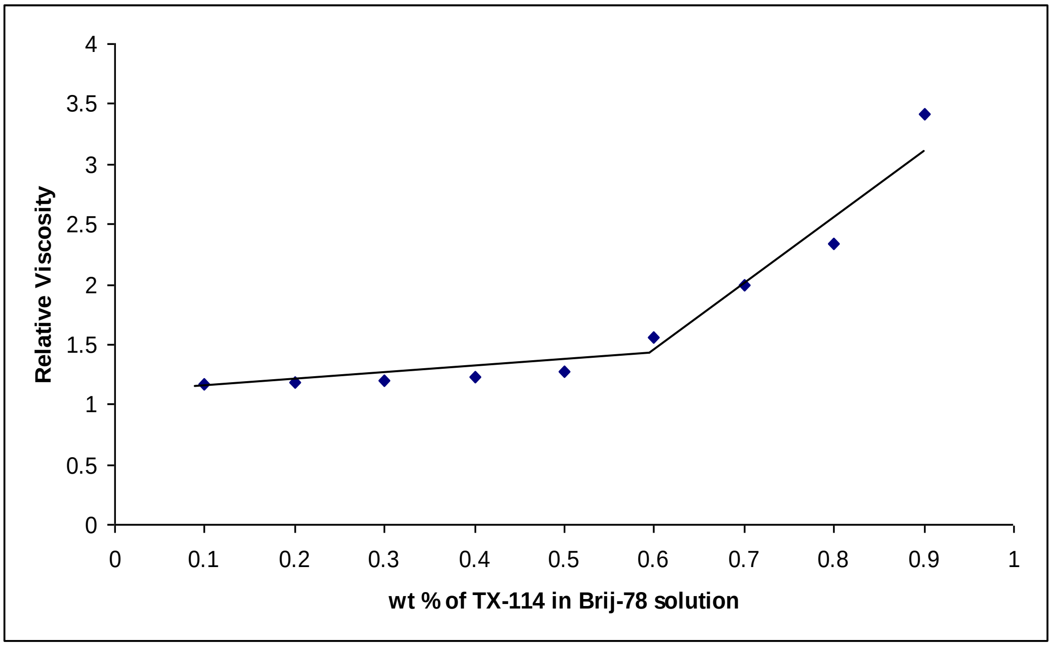


Figure 4.33 Effect of increasing wt % of TX-114 on Relative Viscosity of Brij-78 solution at a decreasing wt % of the polymer.

In all the three nonionic surfactant solutions, there was a slight elevation in relative viscosity at low quantities of TX-114 but at some point of quantity of TX-114, there is steep increase in relative viscosity. The changes were roughly similar as can be seen in Figures 4.31-4.33.

CMC of these nonionic surfactant solutions occurred at a quantity of 0.56 wt % TX-114 in $EO_6PO_{34}EO_6$; 0.5 wt % TX-114 in $EO_{27}PO_{61}EO_{27}$ and 0.5 wt% TX-114in Bj-78 respectively.

4.5.5 Discussion on physic-chemical properties

Cloud points of surfactants indicate the limit of their solubility and therefore its determination is very necessary in judging the quality and characteristic of a surfactant or polymer before use in a process especially where elevated temperature prevails. Cloud point is also used to purify these substances. It is very sensitive to the presence of other substances in the system even at very low concentrations. The additives modify the surfactant-solvent interactions and as a result they change the CMC, the size of the micelles and the phase behavior in the surfactant solution (Soumen and Moulik., 1999). In the cases that were studied, it was confirmed that additives change cloud points of nonionic surfactants hence their CMCs. This, as explained by Soumen and Moulik (1999), could be due to the change in micelle size and phase behavior that takes place in the surfactant solution.

It is also noted that CP of nonionic surfactants decreases with increase in oxidation number of the cation. Inorganic salts may either increase or decrease the cloud point of nonionic surfactants and this is termed as salting-in or salting-out respectively. In the salting-in process, decreased solubility and decreased cloud point results while in salting-out process, increased solubility and cloud point results. Inorganic salts being electrolytes affect electrostatic stabilization of colloids and are detrimental to the physical stability of dispersed dosage forms (Na *et al.*, 1999b). When cloud points of nonionic surfactants are depressed, their applications get limited; therefore those inorganic salts that depress the cloud point of these surfactants reduce the uses of the surfactants. On additing even a small amount of ionic (anionic or cationic) surfactants to nonionic surfactant solutions, the cloud point of the latter raised significantly (Abdullah and Hisham, 1997).

The specific conductivity in all the three solutions is increased by addition of inorganic salts. Since solutions of these salts are electrolytes, the specific conductivity of the nonionic solutions to which they are added is increased. The higher the cation or anion oxidation state, the greater increase in specific conductivity because these ions carry bigger charges. As the concentration of the inorganic salt increases, the number of free ions in solution also increases and this causes an increase in specific conductivity. Also the two ionic surfactant additives (SDS and CTAB) increase the number of free ions in solution when added into solutions of nonionic surfactants hence increase in specific conductivity.

TX-114 is a nonionic surfactant and when added to other nonionic surfactants, it leads to a higher amount of molecular particles in solution which most likely are the cause of depression in specific conductivity. An increase of such molecules in any solution makes movement of any charge conducting particles present difficult hence a reduction in specific conductivity.

This increase that is caused by the inorganic surfactants indicates that in all the three nonionic surfactants, there is an increase in the size of the micelles formed. Most probably, NaCl causes a small increase in micelle size in both P104 and brij-78 solutions which result into a very small increase in relative viscosity. The increase caused by NaCl on relative viscosity of L62 solution is significant which could be implying that there is a greater increase in micelle.

The high increase in relative viscosity in brij-78 solution by SDS indicates that micelle size is caused to increase by addition of SDS in brij-78 solution and this increase is remarkable. The increase in micelle size in either L62 or P104 solutions on adding SDS is very small as shown by a very slight increase in relative viscosity in both. CTAB causes a remarkable increase in micelle size in P104 while in both L62 and brij-78 solutions, the increase are slight.

TX-114 was observed to produce a slightly higher elevation in relative viscosity of brij-78 solution than in the other two nonionic surfactant solutions. The least elevation effect was observed in L62 solution. TX-114 nonionic surfactant causes the same effect in the other nonionic surfactants with respect to relative viscosity of the solutions which means the micelle growth was almost similar in the three surfactant solutions.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The use of benzyl alcohol as a non-polar solvent did not give many thermodynamically stable phases in the two ternary systems: P104/water/oil and L62/water/oil. The P104/water/benzyl alcohol ternary system gave four thermodynamically stable lyotropic liquid crystalline phases which were: normal micellar cubic (l_1), normal hexagonal (H_1), lamellar ($l\alpha$) and reverse hexagonal (H_2). Besides these four phases, it also formed two isotropic liquid solutions: one water-rich (normal micellar, L_1) and one water-lean (reverse micellar, L_2) solutions. The L62/water/benzyl alcohol system forms only one thermodynamically stable lyotropic liquid crystalline phase which is lamellar ($L\alpha$). The copolymer (L62) is completely soluble in benzyl alcohol the reason for the reverse micellar isotropic solution covering the whole range of co-polymer-oil axis.

All three nonionic surfactants gave high Cloud Points in aqueous solutions and those of Brij-78 solution were over 100 ^{0}C throughout. Cloud points of the three nonionic surfactants are depressed with increase in surfactant concentration. Inorganic salts (NaCl, Na_2SO_4) and $AlCl_3$) also depress cloud point. Ionic surfactants, SDS and CTAB, both raised the cloud point of the three nonionic surfactants to above 100 ^{0}C but TX-114, a nonionic surfactant, lowered cloud point of all three nonionic surfactants. Both specific conductivity and relative viscosity were raised by the inorganic salts (NaCl, Na_2SO_4 and $AlCl_3$), the ionic surfactants (SDS and CTAB) and the nonionic surfactant (TX-114).

5.2. Recommendation

Benzyl alcohol is not a good solvents to use in cases where reverse lyotropic liquid crystalline are to be formed. Further research on phase behavior of ternary systems using different solvents for hydrophobic parts of nonionic surfactants should be done in order to establish the best solvents that can produce more thermodynamically stable lyotropic liquid crystalline phases.

Inorganic salts can be added into nonionic surfactant solutions to lower Cloud point, raise specific conductivity and relative viscosity respectively. Ionic surfactants can be used to raise all three physic-chemical properties of nonionic surfactants while lower cloud point and raise both specific conductivity and relative viscosity of nonionic surfactants.

These recommendations are very important to pharmaceutical industries which require the knowledge on physic-chemical properies in drug formulations and manufacture, especially syrup drugs. They will also benefit industries that manufacture emulsions, dispersions and such like products (Soumen and Moulik, 1998).

REFERENCES

Abdullah M. A. and Hisham A. N., (1997). Effect of oilfield chemicals on the cloud point of nonionic surfactants. *Colloids and surfaces A.* Physicochemical and Engineering Aspects **125** :5-8

Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. (1994). Micellization of poly(ethylene oxide)- poly(propylene oxide)-poly(ethylene oxide) triblock copolymers in aqueous solutions: Thermodynamics of copolymer association. *Macromolecules.* **27**: 2414–2425.

Alexandridis, P.; Olsson, U.; Lindman, B. (1995). Self-Assembly of Amphiphilic Copolymers: $EO_{13}PO_{30}EO_{13}$-water-p-xylene system. *Macromolecules*. **28**: 7700-7710.

ALexandridis, P.; Zhou, D.; Khan, A. (1996). Langmuir. **12**: 2690

Alexandridis, P.; Olsson, U.; Lindman, B. (1998). A Record Nine Different Phases (Four Cubic, Two Hexagonal, and One Lamellar Lyotropic Liquid Crystalline and Two Micellar Solutions) in a Ternary Isothermal System of an Amphiphilic Block Copolymer and Selective Solvents (Water and Oil). *Langmuir***. 14***:* 2627-2638

Al-Saden, A. A.; Whateley, T. L. and Florence, A. T. (1982). Poloxamer Association in Aqueous Solution. *J. Colloid Interface Sci.* **90**: 303–309.

Beeslay, A.; Evans, D. F.; Laughlin, J. (1988). Role of Hydrogen Bonding in the Formation of Bile Salt Micelles. *J. Phys. Chem*. **92:** 79.

Benjamin, C. (1995). Structure and Dynamics of Block Copolymer Colloids. *Langmuir Lectures*: *American chemical society*. **11**: 414-421.

Boucher, G. D.; MacDonald, A. C.; Hawrylak, B. E. and Marangoni, G. D. (1998). A Nuclear Magnetic Resonance Investigation of the Micellar Properties of Two-Headed Surfactant Systems: The disodium 4-Alkyl-3-Sulfonatosiccinates.I.Equilibrium Micellar properties. *Can. J. of Chem*. **76**:1266-1273

Callaghan, A.; Doyle, R.; Alexander, E.; Palepu, R. (1993). Thermodynamic properties of micellization and adsorption and electrochemical studies of Hexadecyl pyridinium bromide in binary mixture of 1,2-ethanediol with water. *Langmuir.* **9**: 3422-3426

Campbell, F.C. (2012). Ternary Phase Diagrams—Understanding the Basics, Chapter 10:192-194

Castellano, J. A., (2005). Liquid Gold: The Story of Liquid Crystal Displays and the Creation of an Industry. *World Scientific Publishing*.

Chu, B., (1995). Structure and dynamics of block copolymer colloids. *Langmuir*. **11**: 414–421

Chu, B.and Zhou, Z. (1996). In non-ionic surfactants: polyoxyalkylene block copolymers. V. M., Ed.;Marcel Dekker; New York. **60**: 67

Clogston, J. and Caffrey, M. (2005). Controlling release from the lipidic cubic phase. Amino acids, peptides, proteins and nucleic acids. J. Control. Release 107, 97–111

Collings, P. J.and Hird, M. (1997). Introduction to liquid crystals chemistry and physics, Taylor and Francis, London, UK

De Gennes, P. G. (2001). The physics of liquid crystals, Oxford University Press, UK.

Dolgaleva, K.; Simon, K.; Wei, H.; Svetlana G.; Lukishova, S. H.; Chen, K. S. and Robert W. B. (2008). Enhanced laser performance of cholesteric liquid crystals doped with oligofluorene dye. *Journal of the Optical Society of America.* **25** (9): 1496–1504.

Fendler, J. H. (1982). Interactions and kinetics in Membrane mimetic systems; Membrane Mimetic Chemistry, Wiley, New York

Floudas, G.; Hadjichristidis, N.; Stamm, M.; Likhtman, A. E.; Semenov, A. N. (1997). Microphase Separation in Block Copolymer/Homopolymer Blends. Theory and Experiment. *J. Chem. Phys.* **106**: 3318.

Flores, M. V.; Voutsas, C. E.; Spiliotis, N.; Eccleston, G. M.; Bell, G.; Tassios, D. P.; Halling, P. J. (2001). Critical Micelle Concentrations of Nonionic Surfactants in Organic Solvents. *Journal of Colloid and Interface Science*. **240**: 277-283.

Fontell, K. (1990). Cubic Phases in Surfactant and Surfactant-Like Lipid Systems. *Colloid Polymer Science*. **268**: 264

Furlong, D. N. and Aston, J. R. (1982). Adsorption of Polyoxyethylated Nonyl Phenols at Silica/Aqueous Solution Interfaces: *Colloids Surfaces*. **4**:121-129.

Gabriela, B. (2004). Lyotropic Liquid Crystals. II. Structural Polymorphism, *Romanian Reports in Physics*. **56**: 87-100

Gilbart, W. M.; Ben-Shaul, A.; Roux D. (1994). Micelles, Membranes, Microemulsions and Monolayers. Pringer Verlag, New York.

Gopal, L. (1973). Effects of Alcohols on the Properties of Micellar Systems. III. Elastic and Quasi Elastic Scattering Study. *Journal of Colloid Interface Science*. **84** (1): 206

Gu, T.; Galera-Gomez, P. A. (1995). Clouding of Triton X-114: the Effect of Added Electrolytes on the Cloud Point of Triton X-114 in the Presence of Ionic Surfactants

Hirokazu, H. (1998). Block Copolymers; Generic Phase Behaviour Compared to Surfactant Phase Behaviour. Current Opinion in Colloid and Interface Science. **3**: 264-269

Holmqvist, P.; Alexandridis, P.; Lindman, B. (1997). *Macromolecules*. **30**: 6788.

Holmqvist, P.; Alexandridis, P.; Lindman, B. (1998). *Journal of Physical Chemistry*. **102**: 1149.

Hunter, R. (1987). Foundations of colloid science. (4th ed.). Oxford University Press. Pp 69-96

Hurter, P. N.; Alexandridis, P.; Hatton, T. A. (1995). Solubilization in Surfactant Aggregates; Christian, S. D., Scamehorn, J. F., eds.; Marcel Dekker, New York.

http//www.google/Structure and Properties of Lyotropic Liquid Crystals, (18/11/2013)

Jadhav, V. B.; Patil, A. A. and Patil, T. J. (2012). Influence of Polyelectrolyte on Micellar Behaviour of Non-ionic Surfactant Using Dye Solubilization Technique. *Journal of Chemical and Pharmaceutical Research*. **4(5)**:2400-2403

Karsa, D. R. (1987). Industrial Application of Surfactants. *The Royal Society of Chemistry*. Whitestable Litho Ltd, Kent, UK. PP. 165-180

Khan, A., (1999). Cloud Point of Nonionic Surfactants, Yt & Kolloidkemi Fordjupningskurs

Kipkemboi, P.; Ali, K.; Bjorn, L.; Viveka, A. (2003). Phase Behavior and Structure of Amphiphilic Poly(ethyleneoxide)-Poly(propyleneoxide) Triblock Copolymers $(EO)_4(PO)_9(EO)_4$ and $(EO)_{17}(PO)_{59}(EO)_{17}$ in Ternary Mixtures with Water and Xylene. *Canadian journal of chemistry*. **81**;897-903.

Kopp, V. I.; Fan, B.; Vithana, H. K. M.; Genack, A. Z. (1998). "Low-threshold Lasing at the Edge of a Photonic Stop Band in Cholesteric Liquid Crystals". *Optics Express* **23** (21): 1707–1709.

Lacic, D. D. (1993). Liposomes: From Physics to Applications; Elsevier:Amsterdam

Laurier, L. S.; Elaine, N. S. and Marangoni. D. G., (2003). Surfactants and their Applications. *Annu. Rep. Prog. Chem., Sect. C,* 2003, **99**, 3–48

Luzzati, V.; Mustacchi, H.; Skoulios, A. (1957). "Structure of the Liquid-Crystal Phases of the Soap–water System: Middle Soap and Neat Soap".

Madsen, L. A.; Dingemans, T. J.; Nakata, M.; Samulski, E. T. (2004). Thermotropic Biaxial Nematic Liquid Crystals. *Phys. Rev. Lett.* **92** (14).

Mata, J.; Joshi, T.; Varade, D.; Ghosh, G. and Bahadur, P. (2004). Aggregation behavior of a PEO–PPO–PEO block copolymer + ionic surfactants mixed systems in water and aqueous salt solutions. *Colloids and Surfaces A: Physicochem. Eng. Aspects.* **247**: 1–7

Matsumoto, S. and Kadota, I. (1991). Liquid Crystals. Fundamentals and Applications Kogyochosa-kai, Tokyo, Japan.

Na, G. C.; Stevens, B. O. Yuan, H.; Jack, S.; Brian, S. W.; Rajagopalan, N. (1999a). Cloud Point of Nonionic Surfactants: Modulation with Pharmaceutical Excipients, Pharmaceutical Research. **16** No. 4.

Na, G. C.; Stevens, B. O. Yuan, H.; Rajagopalan, N. (1999b). Physical Stability of Ethyl Diatrizoate Nanocrystalline. Suspension in Steam Sterilization. *Pharmaceutical research*. **16**: 569-574.

Nagamune, N. (1977). The Effect of Added Inorganic Salts on the Micelle Formation of Nonionic Surfactans in Aqueous Solutions. *Bulletin of the Chemical Society of Japan*. **50**:1690-1694.

Prajapati, K. and Patel, S. (2012). Micellization of Surfactants in Mixed Solvent of Different Polarity. Archives of Applied Science Research. **4(1)**:662-668

Qizhen L.; Pengtao L.; Cheng L.:Xigao J.; Dingyi H. and Yang L. (2005). Synthesis and Properties of Lyotropic Liquid Crystalline Copolyamides Containing Phthalazinone Moieties and Ether Linkages. *Polymer*. **46** (16): 6258–6265.

Ramadhan M. S.; Evans, D. F. and Lumry, R. (1983). Solvent Properties of Amphiphilic Compounds. *Journal of Physical Chemistry*. **87**: 4538-4543

Ray, A. and Nemethy, G., (1969). Symposium on Water Structure and Hydrophobic Bonding. Vol. 157 National Meeting of the American Chemical Society, Minneapolis; Minn

Rico, L.and Lattes, A. (1986). Colloidal Surfactants, Some Physico-Chemical Properties, Academic Press New York. *Journal of physical Chemistry*. **90**: 5870

Rosen, M. J. (1978). Surfactants and Interfacial Phenomena: John Wiley and sons, New York.

Rosen, M. J. (1989). Surfactants and Interfacial Phenomena, 2nd Edn. John Wiley and sons, New York.

Sansanwal, P. K. (2006). Effect of Co-Solutes on the Physico-chemical Properties of Surfactant Solutions. *Journal of Scientific and Industrial Research*. **65**:57-64.

Satan, R. M. and Sawant, M. R. (2006). A Study of Performance Properties of Alkyl Poly(glucoside) and Sodium Dodecylsulfate in their Mixed Systems. *Journal for Surface Science and Technology*. **22(1-2)**:75-88

Scamehorn, J. F. (1986). Phenomena in Mixed Surfactant Systems. American Chemical Society Symposium Series 311; Washington DC, P1

Schott, H. (1969). Hydrophile-Lipophile Balance and Cloud Point of Nonionic Surfactants. *Journal of Pharmaceutical Science*. **58**:1443-1449

Schott, H. and Han, S. K. (1977). Effect of Symmetrical Tetraalkylammonium Salts on Cloud Points of Nonionic Surfactants. *Journal of pharmaceutical science*. **66**: 165-168.

Schott, H.; Royce, A. E. (1984). Effect of Inorganic Additives on Solutions of Nonionic Surfactants VI: Further Cloud Point Relations. *Journal of pharmaceutical science*. **73**: 793-799.

Shah, J.C. (2001). Cubic Phase Gels as Drug Delivery Systems. *Advanced Drug Delivery. Rev*. **47**: 229–250

Shaw, J. D. (1989). Colloid ans Surface Chemistry (4th edition). Butterworh-Heineman Ltd. Chapter **4**

Sinha, S.; Bahadur, P.; Jain, N. (2002). Effect of Organic Counter-ions on the Surface Activity, Micellar Formation and Dye Solubilization Behavior of Cationic Surfactants. *Indian Journal of Chemistry*. **41A**: 914-920

Soumen, G.; Moulik, P. S. (1999). The Cloudy Behaviour of Binary Mixtures of

Polyoxyethylene (10) Cetylether (Brij-56) with Polyvinyl Alcohol (PVA) and Methyl Cellulose (MC). *Indian Journal of chemistry*. 38: 201-208.

Soumen, G.; Moulik, P. S. (1999). Clouding Behavior of Binary Mixtures of Triton X100/Tween-80 as well as Tween-20/Brij-35, and the Influences of Ionic Surfactants (SDS, CTAB) and Water Soluble Polymers (PVA and PVP) on their Cloud Points. *Indian Journal of chemistry*. **38A**: 10-16.

Stephen, T. H. (2001). Identification of Lyotropic Liquid Crystalline Mesophases. Handbook of Applied Surface and Colloid Chemistry

Stratton, L. P.; Dong, A.; Manning, M. C.; Carpenter, J. F. (1997). Drug Delivery Matrix Containing Native Protein Precipitates Suspended in a Poloxamer Gel. *Pharmaceutical Science*. **86**:1006-1010.

Svensson, B.; Alexandridis, P.; Olsson, U. (1998). Self-assembly of a Poly[ethylene oxide]-Poly[propylene oxide] Block Copolymer Pluronic P104, ($EO_{27}PO_{61}EO_{27}$) in the Presence of Water and Xylene. *Journal of physical chemistry*. **102**: 7541-7548

Svensson, M.; Paschalis, A.; PerLinse (1999a). Phase Behaviour and Microstructure in Binary Block Copolymer/Selective Solvent Systems. *American Chemical Society*. **32**: 637-645

Svensson, M.; Alexandridis, P.; Linse, P. (1999b). Modeling of the Phase Behavior in Triblock Copolymer/water/oil systems. *Macromolecules*. **32**: 5435-5443.

Travalloni-Louvisse, A. M.; Gonzalez, G. (1988). In D. H. Smith (Ed.). American Chemical Society Symp. Ser. 373. *American Chemical Society*. Washngton DC. Chapter **11.**

Tuzar, Z. and Kratochvil, P. (1993). Block and Graft Copolymers in Solution. *Surface and Colloid Science*; Matjevic, E., Ed.; Plenum Press: New York. Vol. **15**, chap. 1, pp 1-83.

Wu, G.; Ying, Q.; Chu, B. (1994). Self-Assembly of Amphiphilic Block Copolymers: $(EO)_{13}(PO)_{30}(EO)_{13}$-water-*0*-xylene system. *Macromolecules*. **27**: 5758

Yaghmur, A. and Glatter, O. (2009) Characterization and Potential Applications of Nanostructured Aqueous Dispersions. *Adv. Colloid Interface Sci*. 147–148, 333–342

Yamaguchi, A.; Evans, D.;Wei, G. J.; Bloomfield, V. A. (1987). Principles of the Stability of Lyotropic Colloidal Dispersions in Non Aqueous Media. *J. Phys. Chem*. **87**: 3537.

Yang, L. and Alexandridis, P. (2000). Polyoxyalkylene Block Copolymers in Formamide-Water Mixed Solvents: Micelle Formation and Structure tudied by Small-Angle Neutron Scattering. *Langmuir*. **16**: 4819–4829.

Zhou, D.: Alexandridis, P. and Khan, A. (1996). Self-Aassembly in a Mixture of two Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) Copolymer in Water. *Journal of colloid and interfacial science*. **183**: 339-350.

Appendices

Appendix I: Cloud point, Specific Conductivity and Relative Viscosity of L62 aqueous solutions

Conc. of L-62 (molL^{-1})	CP of L-62 (^{0}C)	Specific Conductivity of L-62 (µS)	Relative Viscosity of L-62
0.001	38	33.2	1.016
0.002	36	33.5	1.018
0.004	32	35.5	1.047
0.008	27	63	1.094
0.01	25	-	1.172
0.02	23	-	1.266
0.05	22	.-	1.500

Appendix II: Cloud Point, Specific Conductivity and Relative Viscosity of P104 aqueous solutions

Conc. of P104 (molL^{-1})	CP of P104 (^{0}C)	Specific Conductivity of P104 (µS)	Relative Viscosity of P104
0.001	82	21	1.047
0.002	80	26	1.100
0.004	75	50	1.211
0.008	72	77	1.313
0.01	70	-	1.578
0.02	68	-	1.745
0.05	65	-	1.987

Appendix III: Specific Conductivity and Relative Viscosity of aqueous solution of Brij-78

Conc. of Brij-78 ($molL^{-1}$)	Specific Conductivity of Brij-78 (μS)	Relative Viscosity of Brij-78
0.001	26	1.025
0.002	22	1.031
0.004	14	1.075
0.008	30	1.116
0.01	46	1.227
0.02	72	1.359
0.05	130	1.494

Appendix IV: Effect of NaCl on CP of L62, P104 and Brij-78

Conc. Of NaCl in solution ($molL^{-1}$)	wt $^0/_0$ of Surfactant	CP of L-62 in NaCl (^0C)	CP of P-104 in NaCl (^0C)	CP of Brij-78 in NaCl (^0C)
0.050	1.0	28.5	71	42
0.075	1.0	27.5	70	44
0.1	1.0	26.0	68	45
0.25	1.0	24.5	67	46
0.50	1.0	24.1	62	47.2
0.75	1.0	19.5	60	47.7
1.0	1.0	17.0	57	48
1.50	1.0	12.5	55	48.2

Appendix V: Effect of Na_2SO_4 on CP of L62, P104 and Brij-78

Conc. of Na_2SO_4 (molL^{-1})	wt $^0/_0$ of Surfactant	CP of L-62 in Na_2SO_4 (^{0}C)	CP of P-104 in Na_2SO_4 (^{0}C)	CP of Brij-78 in Na_2SO_4 (^{0}C)
0.01	1.0	70	74	45
0.050	1.0	70	72	45.7
0.1	1.0	69	71	46.5
0.25	1.0	67	70	47
0.50	1.0	62	68	47.4
0.75	1.0	60	65	47.5
1.0	1.0	57	55	48
1.50	1.0	55	35	49

Appendix VI: Effect of $AlCl_3$ on CP of L62, P104 and Brij-78

Conc. of $AlCl_3$(m/l)	wt $^0/_0$ of Surfactant	CP of L-62 in $AlCl_3$ (^{0}C)	CP of P-104 in $AlCl_3$ (^{0}C)	CP of Brij-78 $AlCl_3$ (^{0}C)
0.01	1.0	27	70	48
0.050	1.0	26	65	48.2
0.1	1.0	25.5	56	48.5
0.25	1.0	23	47	49
0.50	1.0	18	45	49.4
0.75	1.0	14	39	49.6
1.0	1.0	9	32	50
1.50	1.0	6	23	50.5

Appendix VII: Effect of SDS on CP of L62, P104 and Brij-78

Conc. of SDS (molL^{-1})	wt % of Surfactant	CP of mixture of L-62 and SDS (^{0}C)	CP of mixture of P-104 and SDS (^{0}C)	CP of mixture of Brij-78 and SDS (^{0}C)
0.01	1.0	□ 100	□ 100	□ 100
0.02	1.0	,,	,,	,,
0.03	1.0	,,	,,	,,
0.04	1.0	,,	,,	,,
0.05	1.0	,,	,,	,,
0.075	1.0	,,	,,	,,

Appendix VIII: Effect of CTAB on CP of L62, P104 and Brij-78

Conc. of CTAB ($molL^{-1}$)	wt % of Surfactant	CP of mixture of L-62 and CTAB (^{0}C)	CP of mixture of P104 and CTAB (^{0}C)	CP of mixture of Brij-78 and CTAB (^{0}C)
0.01	1.0	□ 100	□ 100	□ 100
0.02	1.0	,,	,,	,,
0.03	1.0	,,	,,	,,
0.04	1.0	,,	,,	,,
0.05	1.0	,,	,,	,,
0.1	1.0	,,	,,	

Appendix VIX: Effect of TX-114 on CP of P104 and Brij-78

wt % of TX-114	wt % of surfactant	CP of mixture of P-104 and TX-114 (^{0}C)	CP of mixture of Brij-78 and TX-114 (^{0}C)
0.10	0.90	68	□100
0.20	0.80	65	
0.30	0.70	63	97
0.40	0.60	62	90
0.50	0.50	61	81
0.60	0.40	59	72
0.70	0.30	56	60
0.80	0.20	40	48
0.90	0.10	31	37

Appendix X: Effect of NaCl on Specific Conductivity (µS) of L62, P104 and Brij-78

Conc. of NaCl (m/l)	wt $^0/_0$ of Surfactant (g)	Specific Conductivity of L-62 in NaCl (µS)	Specific Conductivity of P-104 in NaCl (µS)	Specific Conductivity of Brij-78 in NaCl (µS)
0.01	1.0	0.24	0.6	0.20
0.050	1.0	0.68	1.05	0.40
0.10	1.0	1.2	1.47	0.70
0.25	1.0	1.92	4.5	1.46
0.50	1.0	3.62	10.4	3.20
0.75	1.0	5.6	18.6	9.4
1.0	1.0	11.4	28.5	14.60

Appendix XI: Effect of Na_2SO_4 on Specific Conductivity (µS) of L62, P104 and Brij-78

Conc. of Na_2SO_4(m/l)	wt $^0/_0$ of Surfactant	SC of L-62 in Na_2SO_4 (µS)	SC of P-104 in Na_2SO_4 (µS)	SC of Bj-78 in Na_2SO_4 (µS)
0.01	1.0	0.39	0.81	0.81
0.050	1.0	1.35	1.76	1.45
0.1	1.0	1.56	2.86	2.25
0.25	1.0	2.85	8.48	2.35
0.50	1.0	6.48	15.6	9.44
0.75	1.0	11.52	29.75	17.6

Appendix XII: Effect of $AlCl_3$ on Specific Conductivity (µS) of L62, P104 and Brij-78

Conc. of $AlCl_3$ ($molL^{-1}$)	wt $^0/_0$ of Surfactant	Specific Conductivity of L-62 in $AlCl_3$ (µS)	Specific Conductivity of P-104 in $AlCl_3$ (µS)	Specific Conductivity of Brij-78 in $AlCl_3$ (µS)
0.025	1.0	1.20	1.12	1.13
0. 05	1.0	2.16	2.24	2.18
0. 075	1.0	3. 2	3.30	3.48
0. 1	1.0	4.80	4.85	5.38
0.2	1.0	6.20	7.20	8.56
0.4	1.0	8.40	9.10	12.80
0.5	1.0	10.80	12.60	14.40
1.0	1.0	16.8	18.42	20.90
1.5	1.0	27.5	29.64	32.80

Appendix XIII: Effect of SDS on Specific Conductivity (µS) of L62, P104 and Brij-78

Conc. of SDS ($molL^{-1}$)	wt % of Surfactants	Specific Conductivity of mixture of BriJ-78 and SDS (µS)	Specific Conductivity of mixture of L-62 and SDS (µS)	Specific C of mixture of P-104 and SDS (µS)
0.01	1.0	0.33	0.79	0.64
0.025	1.0	0.81	1.24	0.78
0.04	1.0	1.54	2.45	2.2
0.05	1.0	1.94	5.2	2.9
0.075	1.0	3.14	13	7.48
0.1	1.0	5.10	20.5	10.67

Appendix XIV: Effect of CTAB on Specific Conductivity (µS) of L62, P104 and Brij-78

Conc. of CTAB (molL^{-1})	wt % of Surfactants	Specific Conductivity of mixture of L-62 and CTAB (µS)	Specific Conductivity of mixture of P-104 and CTAB (µS)	Specific Conductivity of mixture of Brij-78 and CTAB (µS)
0.01	1.0	0.8	0.71	0.52
0.02	1.0	1.38	1.12	0.93
0.03	1.0	1.96	1.32	2.05
0.04	1.0	2.37	1.71	2.59
0.05	1.0	2.89	2.04	3.48
0.075	1.0	4.32	2.78	7.8
0.1	1.0	6.00	3.52	12.5

Appendix XV: Effect of TX-114 on Specific Conductivity (µS) of L-62, P-104 and Brij-78 solutions

wt% of TX-114	wt% of surfactant	Specific Conductivity of mixture of TX-114 and L-62 (µS)	Specific Conductivity of mixture of TX-114 and P-104 (µS)	Specific Conductivity of mixture of TX-114 and Bj-78 (µS)
0.10	0.90	59.8	66	48.9
0.20	0.80	55.6	64	44.8
0.30	0.70	47.8	59	43.1
0.40	0.60	40.6	54	40.8
0.50	0.50	34.8	48	37.8
0.60	0.40	37.8	40	34.6
0.70	0.30	38.8	35	3.3
0.80	0.20	42.8	31	28.6
0.90	0.10	45.0	27	27.1

Appendix XVI: Effect of NaCl on Relative Viscosity of L62, P104 and Brij-78 solutions

Conc. of NaCl molL^{-1}	wt % of Surfactant	Relative Viscosity. L-62 in NaCl	Relative Viscosity P-104 in NaCl	Relative Viscosity of Brij-78 in NaCl
0.005	1.0	1.1156	1.1125	1.1016
0.01	1.0	1.1156	1.1130	1.1024
0.02	1.0	1.1156	1.1140	1.1042
0.050	1.0	1.1156	1.1154	1.1051
0.1	1.0	1.1156	1.1156	1.1067
0.25	1.0	1.125	1.1186	1.108
0.50	1.0	1.1406	1.1125	1.1094
0.75	1.0	1.1641	1.1156	1.1250
1.0	1.0	1.2031	1.1156	1.1344
1.50	1.0	1.3031	1.1406	1.1438

Appendix XVII: Effect of Na_2SO_4 on Relative Viscosity of L-62, P-104 and Brij-78 solutions

Conc. of Na_2SO_4 molL^{-1}	wt % of Surfactant	Relative Viscosity of L62 in Na_2SO_4	Relative Viscosity of P104 in Na_2SO_4	Relative Viscosity of Brij-78 in Na_2SO_4
0.010	1.0	1.1125	1.1484	1.0719
0.020	1.0	1.1141	1.1531	1.0836
0.050	1.0	1.1165	1.1619	1.0979
0.10	1.0	1.1188	1.1712	1.1000
0.50	1.0	1.1188	1.1800	1.1094
0.75	1.0	1.1256	1.1925	1.1219
1.0	1.0	1.1406	1.2656	1.1281

Appendix XVIII: Effect of $AlCl_3$ on Relative Viscosity of L-62, P-104 and Brij-78 solutions

Conc. of $AlCl_3$ ($molL^{-1}$)	wt % of Surfactant	Relative Viscosity of L62 in $AlCl_3$	Relative Viscosity of P104 in $AlCl_3$	Relative Viscosity of Brij-78 in $AlCl_3$
0.01	1.0	1.1156	1.1563	1.11562
0.02	1.0	1.1156	1.1719	1.11875
0.05	1.0	1.1203	1.2031	1.14062
0.075	1.0	1.1219	1.2109	1.14450
0.1	1.0	1.1219	1.2156	1.1906
0.25	1.0	1.1219	1.3281	1.3094
0.5	1.0	1.1281	1.5313	1.5000
0.75	1.0	1.1469	1.8063	1.8315
1.0	1.0	1.1656	2.1563	2.2094
1.5	1.0	1.1813	3.3844	3.2266

Appendix XIX: Effect of SDS on Relative Viscosity of L-62, P-104 and Brij-78 solutions

Conc. of SDS ($molL^{-1}$)	wt % of surfactant	Relative Viscosity of mixture L62 and SDS	Relative Viscosity of mixture P104 and SDS	Relative Viscosity of mixture Brij-78 and SDS
0.005	1.0	1.084	1.14	1.116
0.01	1.0	1.096	1.15	1.116
0.02	1.0	1.119	1.163	1.185
0.03	1.0	1.119	1.178	1.234
0.04	1.0	1.124	1.184	1.303
0.05	1.0	1.135	1.192	1.512
0.075	1.0	1.154	1.209	1.654
0.1	1.0	1.164	1.222	1.821

Appendix XX: Effect of CTAB on Relative Viscosity of L-62, P-104 and Brij-78 solutions

Conc. of CTAB (molL^{-1})	wt % of surfactant	Relative Viscosity of mixture of L62 and CTAB	Relative Viscosity of mixture of P104 and CTAB	Relative Viscosity of mixture of Brij-78 and CTAB
0.005	1.0	1.094	1.172	1.141
0.01	1.0	1.103	1.175	1.149
0.02	1.0	1.147	1.219	1.163
0.03	1.0	1.181	1.234	1.172
0.04	1.0	1.198	1.303	1.188
0.05	1.0	1.234	1.438	1.213
0.075	1.0	1.313	1.484	1.231
0.1	1.0	1.406	1.91	1.25

Appendix XXI: Effect of TX-114 on Relative Viscosity of L-62, P-104 and Brij-78 solutions

wt % of TX-114	wt % of Surfactant	RV of mixture of TX-114 and L62	RV of mixture of TX-114 and P104	RV of mixture of TX-114 and Brij-78
0.10	0.90	1.125	1.166	1.172
0.20	0.80	1.132	1.187	1.189
0.30	0.70	1.157	1.192	1.203
0.40	0.60	1.187	1.202	1.235
0.50	0.50	1.266	1.235	1.272
0.60	0.40	1.369	1.433	1.572
0.70	0.30	1.516	1.783	1. 986
0.80	0.20	1.719	1.974	2.342
0.90	0.10	2.047	2.872	3.414