



<http://researchspace.auckland.ac.nz>

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.

A Study of Triton X Series
Nonionic Surfactant Solutions

A Thesis Presented to the University of Auckland
for the Degree of Doctor of Philosophy

by

Lijun Qiao

Department of Chemistry
November 1996

Dedications

In memory of my beloved father **Jishan Qiao**

Table of Contents

	page
Acknowledgment	ix
Abstract	xi
Index of Tables	xv
Index of Figures	xviii
Chapter 1 : Introduction	1
1.1. Background	1
1.1.1. Surfactants	1
1.1.2. Triton X series surfactants	5
1.1.3. The properties of aqueous Triton X surfactant solutions	8
1.1.4. The association of Triton X surfactants with some additives in aqueous solutions	11
1.1.5. Liquid crystalline states of surfactant solutions	13
1.2. Aims of the study	16
References	20
 Chapter 2 : Theories and Principles of Techniques	 24
2.1. Theories	24
2.1.1. The transition - state theory for viscous flow	24

2.1.2. The complexation between dyes and Triton X series nonionic surfactants	31
2.1.3. Cloud point and flocculation	34
(1) Cloud point	34
(2) Flocculation	36
2.1.4. Depletion flocculation	37
2.1.5. Micelles of polysoaps	38
2.1.6. Surfactant parameter and spontaneous mean curvature	42
2.2. Principles of techniques	45
2.2.1. Viscometry	45
2.2.2. Density measurement	46
2.2.3. Diffusion coefficient determination	48
2.2.4. Optical microscopy with cross - polarised lens	50
2.2.5. Surface tension measurement	51
(1) Ring - detachment method	51
(2) Capillary method	51
2.2.6. Cloud point measurement	53
2.2.7. Vapour pressure osmometry	54
References	56
Chapter 3 : Mass Transport in Triton X Nonionic Surfactant	
Solutions	59
3.1. Introduction	59
3.2. Experimental	61
3.3. Results and discussion	63

3.4. Conclusions	80
References	81
Chapter 4 : The Complexation Between Dyes and Triton X	
Series Nonionic Surfactants	83
4.1. Introduction	83
4.2. Experimental	85
4.3. Results and discussion	88
4.3.1. CMC determination on the solutions	88
4.3.2. The dye - surfactant interactions	91
(1) Methylene Blue - Triton X systems	91
(2) Phenosafranine - Triton X systems	95
4.4. Conclusion	100
Reference	101
Chapter 5 : The Interactions Between Triton X Series Surfactants	
and Polyethylene Glycol in Aqueous Solutions	103
5.1. Introduction	103
5.2. Experimental	111
5.2.1. Materials	111
5.2.2. Surface tension measurements	111
5.2.3. Cloud point and phase separation	112
5.2.4. Determination of Triton X and PEG in the separate phases	112
5.3. Results and discussion	116
5.3.1. The influence of PEG on the surface tension of	
Triton X aqueous solutions	116

5.3.2. The influence of PEG on cloud point of Triton X aqueous solutions	124
5.4. Conclusion	144
References	146
Chapter 6 : Investigations of the Phase Behaviour of Nonionic Triton X - 100 Surfactant Using Microscopy	149
6.1. Introduction	149
6.2. Experimental	156
6.2.1. Materials and instruments	156
6.2.2. Phase diagrams	157
(1) Two - component phase diagrams	157
(2) Three - component phase diagrams	157
6.3. Results and discussion	158
6.3.1. The liquid crystalline states and structures in Triton X aqueous solutions	158
6.3.2. The influence of additives on the liquid crystalline structures	172
6.4. Conclusion	179
References	181
Chapter 7 : Other Studies of Triton X Surfactant Solutions	183
7.1. Introduction	183
7.1.1. The activity coefficients of water and methanol as solvents in Triton X-100 solutions	184
7.1.2. ^1H NMR spectrometric measurements of Triton X-100 aqueous solutions over the whole concentration range	185

7.1.3. Conductance of electrolytes in Triton X aqueous solutions	186
7.2. Experimental	188
7.2.1. Materials	188
7.2.2. Instruments	188
7.3. Results and discussion	190
7.3.1. Activity coefficients of solvents in Triton X-100 aqueous solutions	190
7.3.2. The changes of ^1H chemical shifts of Triton X-100 over the whole concentration range	194
7.3.3. The effects of Triton X surfactants on the conductance of aqueous electrolyte solutions	199
7.4. Conclusion	204
References	206

Acknowledgments

I am very pleased to express my heartily thanks to my supervisor, Dr. Allan J. Easteal for his guidance, patience and encouragement. These have been supporting me to realise my dream to earn a Ph.D in my life. Five years ago, I, a Chinese student, came to New Zealand, a beautiful but strange land, with a poor English to look for a study opportunity. After several failures in applications, I fortunately met Dr. Easteal. He received me and gave me a lot of help to pick up in the new environment. Words can not be enough to express my gratitude to him.

A special thank is given to Mr. Peter Buchanan, the technician of physical chemistry section of the Chemistry Department, for his unselfish support and helpful discussion in almost every part of my work.

The thanks can also be extended to all the staffs of the Chemistry Department, especially Drs. John Seakins, Michael Liddle, Diana Siew, Mr. Michael Walker and Mrs. Catherine Hobbs and Mrs. Sue Courtney of Geology Department for their contributions in some ways to my research.

I am very grateful to the New Zealand government for granting me a MERT Scholarship, and to the Chemistry Department for providing a Teaching Fellowship which financially support me for a long period of time.

Finally my family gives a lot of support and encouragement to me during my years in the university. I wish to take the chance to thank my wife Lana Xiaohua Wang and my sons Yang and Daniel for their love, support, and patience. I would like to thank my parents for their love and education to me. My thanks are also to my sister Helen and brother-in-law David Jiang for their support to my study.

Abstract

This work contains some fundamental investigations on Triton X series nonionic surfactants from different aspects. Techniques, such as viscometry, densimetry, diffusion measurement, ultra-violet spectrophotometry, differential scanning calorimetry, surface tension measurement and optical microscopy were employed to acquire the information. Some theoretical analyses were given to the results of these measurements.

Triton X surfactants show different properties when they dissolve in different solvents. Aggregation can occur in some solvents, depending on the interactions between solvent and solute. The addition of a surfactant to a solvent will give rise to a solute-solvent interaction and change the solute-solute and solvent-solvent interactions as well. From mass transport properties of the surfactant solutions, these interactions were studied and the contributions to them from each species of the solutions were calculated with a transition-state theory model which is usually used for small molecule systems. Under some reasonable assumptions, a new theoretical method was set up and was able to give a reasonable explanation for the experimental results.

The surfactants can also associate with some dyes in both polar and apolar media. The ultra-violet spectra of the surfactant-dye solutions show that surfactant-dye complexes might be formed in the polar and apolar media where the surfactants form regular and reversed micelles respectively. The mechanism of the complexation reactions was studied with equilibrium theory and the charge-transfer nature of the association between the surfactant and dye revealed.

The surface tension and cloud point changes due to the addition of polyethylene glycol were determined to discover the interaction between the water-soluble polymer PEG and the surfactants at the air-solution interface and in the bulk solutions respectively. The mass distribution of the two materials between the two phases produced in the segregation (at the cloud point) of the solutions were determined by their ultra-violet adsorption spectra and densities. The analysis of the cloud point changes was given with the new concepts of polysoap and depletion flocculation. The results show that the size of the micelles, the length of the polymer chains, and the structures of the intra - chain micelles can change the mechanisms of polymer-surfactant interaction and influence the properties of the polymer / surfactant solutions.

In a certain range of concentrations, the surfactants aqueous solutions can form liquid crystalline structures which can be observed under a cross-polarised microscope and determined by differential scanning calorimetry.

The phase diagrams and their variations with additions of the third component, such as xylene, polyethylene glycol and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ have been determined. The effects of temperature and each of the additives on the ordered structures were analysed separately in the light of concepts of spontaneous mean curvature and "salting out" effect.

Osmotic coefficients of the surfactant aqueous and methanol solutions were determined with a vapour pressure osmometer, and the activity coefficient of the solvent can be calculated with the osmotic coefficients. The change of the activity coefficient with increase of surfactant concentration shows the interactions of the surfactant with the solvent. In aqueous solution, the addition of surfactant frees the solvent molecules, leading to an activity coefficient larger than 1. In methanol solution, the surfactant addition reduces the fugacity of methanol molecules, resulting in an activity coefficient less than 1.

Chemical shift changes of protons of the surfactant molecules in the ^1H NMR spectra show some information about the configuration of the chains, hydration, and phase structure of the solution system when the surfactant concentration changes over the whole concentration range. From 40% w/w the associated water molecules begin to be lost, and the association number ratio of water molecules and the ethylene oxide unit of the surfactant is 4 : 1.

Electric conductance of electrolytes in the surfactant aqueous solutions are reduced by the addition of the surfactants. The reduction is more significant for large size cations, and the longer the EO chain of the surfactant, the larger the reducing effect on conductance.

Index of Tables

	page
Table 1.1 Comparison between anionic surfactants and polyoxyethylene - type nonionic surfactants.	4
Table 1.2 Some physical properties of Triton X surfactants.	7
Table 1.3 The CMC values of Triton X surfactant aqueous solutions.	9
Table 3.1 Relative densities and viscosities for Triton X surfactants in water.	65
Table 3.2 Relative densities and viscosities for Triton X surfactants in methanol.	66
Table 3.3 Tracer diffusion coefficients of Triton X-100 in 0.01 mol L ⁻¹ solution in water and methanol.	67
Table 3.4 Relative densities and viscosities for solutions of Triton X-100 in methanol - water mixtures.	68
Table 3.5 Viscosity B coefficients and values of $\Delta\mu^{\ominus\ddagger}_3$ for solutions of Triton X-100 in methanol - water mixtures.	69
Table 3.6 Values of $\Delta G^{\ominus}_3(1\rightarrow 1')$ for Triton X surfactant solutions.	69

Table 4.1	The CMC values for Triton X surfactants in water and mixed solvents of cyclohexane and n - hexanol (4:1 v / v).	89
Table 4.2	The absorbance data for Triton X surfactant - Methylene Blue dye solutions at 516 nm.	93
Table 4.3	The equilibrium constants of Triton X - MB complexes in mixed solvents of cyclohexane and n - hexanol (4:1 v / v).	94
Table 4.4	The absorbance data for Triton X surfactants - Phenosafranine dye solutions at 534 nm.	98
Table 4.5	The equilibrium constants of Triton X - Phenosafranine complexes in water.	99
Table 5.1	The data for ultra - violet absorption calibration of Triton X aqueous solutions.	113
Table 5.2	The data for density calibration curves of Triton X-100 and PEG.	114
Table 5.3	The data for surface tensions of PEG aqueous solutions(25°C).	119
Table 5.4	The data for surface tensions of Triton X-100 / PEG(1000) solutions.	122
Table 5.5	The data for the cloud point changes of Triton X surfactant aqueous solutions.	127
Table 5.6	Triton X and PEG concentration ratios between the upper and lower phases.	129

Table 5.7	The data for the effects of PEG on cloud point of Triton X-114 surfactant aqueous solutions.	131
Table 5.8	The data for the effects of PEG on cloud point of Triton X-100 surfactant aqueous solutions.	138
Table 5.9	The data for the effects of PEG on cloud point of Triton X-102 surfactant aqueous solutions.	135
Table 7.1	The molal osmotic coefficients of water and methanol in Triton X-100 solution at 30°C.	191
Table 7.2	The solvent activity coefficients of Triton X-100 solutions at 30 °C.	192
Table 7.3	Proton chemical shift(expressed as ppm, relative to DSS) for Triton X-100 aqueous solutions.	197
Table 7.4	The conductance of electrolyte / Triton X-114 aqueous solutions.	200
Table 7.5	The conductance of electrolyte / Triton X-100 aqueous solutions.	201
Table 7.6	The conductance of electrolyte / Triton X-102 aqueous solutions.	202
Table 7.7	The rates of decrease of conductance for electrolyte / Triton X aqueous solutions.	203

Index of Figures

	page
Figure 1.1 Industrial applications of surfactant materials.	2
Figure 1.2 Molecular structure of Triton X surfactants.	5
Figure 1.3 The changes of micellar shape with the increase of surfactant concentration in water.	13
Figure 1.4 Two most common types of lyotropic liquid crystalline structures.	14
Figure 2.1 The interactions among particles in a colloidal system.	39
Figure 2.2 The structures of intra-chain micelles of polysoap.	40
Figure 2.3 Three possible configurations of polysoap.	41
Figure 2.4 The curvature of hydrophilic / hydrophobic interface in a micelle	44
Figure 2.5 Cannon-Ubbelohde type viscometer.	46
Figure 2.6 Magnetically stirred diaphragm cell for diffusion coefficient measurement.	50
Figure 2.7 Capillary method for surface tension measurement.	53
Figure 3.1 The particle movement in viscous fluid.	63
Figure 3.2 The viscosity B coefficient for Triton X surfactant aqueous solution at two temperatures.	72
Figure 3.3 A schematic diagram of viscous energy - distance for a water molecule in Triton X surfactant aqueous solutions.	73

- Figure 3.4** The viscosity B coefficient for Triton X surfactants in methanol. 75
- Figure 3.5** A schematic diagram of viscous energy - distance for a methanol molecule in Triton X surfactant methanol solutions. 76
- Figure 3.6** The CMC values of Triton X-100 in water - methanol mixed solvents. 77
- Figure 3.7** The viscosity B coefficient changes with methanol content in Triton X-100 aqueous solutions. 78
- Figure 3.8** $\Delta\mu^{\ominus\#}_3$ decrease with increase of methanol content in the solutions. 79
- Figure 4.1** The structures of the two dyes used in the complexation reactions. 87
- Figure 4.2** The change of relative absorptions at 650 nm and 516 nm along with the increase of surfactant concentration. 90
- Figure 4.3** The UV absorption spectra of Triton X-100 / MB in mixtures of cyclohexane and n-hexanol. 92
- Figure 4.4** The UV absorption spectra of Triton X-100 / PSF in water. 97
- Figure 5.1** A conceptual model for study of surfactant - polymer interactions. 106
- Figure 5.2** The UV adsorption calibration curve for Triton X-100 aqueous solutions. 113
- Figure 5.3** Density calibration curves for Triton X-100 and PEG aqueous solutions. 115

- Figure 5.4** The demonstration of polymer molecules at the air - solution interface. 118
- Figure 5.5** The surface tensions of aqueous solutions of PEG with different molar mass. 118
- Figure 5.6** The surface tension of the surfactant aqueous solutions changes when PEG polymer is added. 121
- Figure 5.7** The cloud point change for aqueous solutions of different Triton X surfactants (10% w/w.). 125
- Figure 5.8** The influence of concentration on the cloud point of Triton X surfactant aqueous solutions. 126
- Figure 5.9** The effect of PEG on the cloud point for Triton X-114 aqueous solutions. 130
- Figure 5.10** The effect of PEG on the cloud point for Triton X-100 aqueous solutions. 132
- Figure 5.11** The effect of PEG on the cloud point for Triton X-102 aqueous solutions. 134
- Figure 5.12** Possible configuration of the polysoap which is favoured for the attraction among the micelles. 137
- Figure 5.13** Surfactant monomer exchange between adjacent intra - chain micelles. 138
- Figure 5.14** A schematic energy / force - distance diagram showing the interaction between two particle in the solutions. 142

- Figure 6.1** The DSC diagram for Triton X-100 aqueous solution (40% w / w.). 159
- Figure 6.2** The phase diagram for Triton X-100 aqueous solutions from DSC data. 160
- Figure 6.3** The phase diagram for Triton X-100 aqueous solutions from microscopic observation. 161
- Figure 6.4** Classical textures of the hexagonal and lamellar phases. 161-162
- Figure 6.5(a)** Lamellar phase texture of 55% w / w. Triton X-100 aqueous solution. 163
- Figure 6.5(b)** Hexagonal phase texture of 35% w / w. Triton X-100 aqueous solution. 163
- Figure 6.5(c)** Lamellar phase texture of 6 % w / w. PEG1000 in Triton X-100 aqueous solution (50% w / w.). 164
- Figure 6.5(d)** Hexagonal phase texture of 2 % w / w. Peg1000 in Triton X-100 aqueous solution (40% w / w.). 164
- Figure 6.5(e)** Lamellar phase texture of 50% p - xylene in Triton X-100 aqueous solution (50% w / w.). 165
- Figure 6.5(f)** Hexagonal phase texture of 5 % p - xylene in Triton X-100 aqueous solution (35% w / w.). 165
- Figure 6.5(g)** Lamellar phase plus solid crystal texture of 50% w / w. BaCl₂ in Triton X-100 aqueous solution (50% w / w.). 166

- Figure 6.5(h)** Hexagonal phase texture of 5 % w / w. BaCl₂ in Triton X-100 aqueous solution (35% w / w.). 166
- Figure 6.6** The viscosity changes of Triton X-100 aqueous solution with increase of concentration (25°C). 169
- Figure 6.7** The phase diagram for Triton X-100 / PEG1000 aqueous solution at 25°C. 173
- Figure 6.8** The phase diagram for Triton X-100 - water - xylene system at 25°C. 177
- Figure 6.9** The phase diagram of Triton X-100 - water - BaCl₂ 2H₂O at 25°C. 178
- Figure 7.1** The activity coefficients of water and methanol in Triton X-100 solutions (30°C). 193
- Figure 7.2** ¹H NMR spectrum of Triton X-100 aqueous solution (25°C). 196
- Figure 7.3** Chemical shift of protons of Triton X-100 aqueous solutions over the whole concentration range (25°C). 198
- Figure 7.4** The conductance of NaCl (0.2 mole dm⁻³) / Triton X aqueous solutions. 203