



**OPTIMISATION OF WATER-IN-OIL MICROEMULSION  
FORMULATION STABILISED BY NONYLPHENOL  
ETHOXYLATED PHOSPHATE ESTER**

**JOHAN MDHLOVU**

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**Department of Chemistry  
Faculty of Natural and Agricultural Sciences  
University of Pretoria  
Pretoria**

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## ABSTRACT

Water-in-oil (w/o) microemulsion systems, stabilised by either an anionic surfactant or a cationic surfactant were studied. The anionic system consisted of ethoxylated nonylphenol phosphate esters (Atpol), Shellsol oil and an alcohol. These microemulsions tolerated an increase in ionic strength of the water phase up to a point: Beyond this point no microemulsion could be obtained. However, adding amine salts, e.g. diethanolamine nitrite, improved the emulsification of the aqueous phase. Increasing the alcohol (cosurfactant) chain length up to octanol also increased the uptake of the aqueous phase. Thus octanol yielded the best results in terms of emulsifying large volumes of the water-phase, particularly at high salt concentrations. A key objective was to prepare stable microemulsions with high nitrite content. The maximum microemulsion nitrite contents (expressed as  $\text{NaNO}_2$  equivalent by mass) achieved were:

- About 10% when a 30%  $\text{NaNO}_2$  solution was emulsified
- 23% when neat diethyl ethanolamine nitrite (DEEAN) was solubilized, and
- 23% for mixtures of diethanolamine nitrite (DEtOHAN) and  $\text{NaNO}_2$  in water.

The cationic microemulsion system was based on the double-chain cationic surfactant, didodecyldimethyl ammonium chloride (DDAC). In this case the solubilization of the following acetate salts were investigated: ammonium, sodium, magnesium, zinc and manganese. As with the Atpol system, it was found that increasing the ionic strength is detrimental to microemulsification of the aqueous phase. In the DDAC system, an increase in the alcohol chain length beyond butanol led to reduced aqueous phase uptake. Thus the natures and concentrations of the surfactant and the cosurfactant as well as the ionic strength of the aqueous phase determine the stability and the emulsification of large volumes of aqueous phase. In general there is an optimum ionic strength at which the salt content of the microemulsion formulation is maximised.

## KEYWORDS

Surfactant, water-in-oil microemulsion, didodecyldimethyl ammonium chloride, nonylphenol ethoxylated phosphate ester, amine, alcohol, ionic strength.

## OPSOMMING

Water-in-olie (w/o) mikroemulsies sisteme, gestabiliseer deur óf 'n anioniese óf 'n kationiese surfaktant is bestudeer. Die anioniese sisteem is saamgestel uit etoksileerde nonielfenolfosfaatesters (Atpol), Shellsol olie en 'n alkohol. Hierdie mikroemulsies verdra 'n toename in die ioniese sterkte van die waterfase tot op 'n punt: Bokant 'n bepaalde vlak vorm daar nie meer 'n mikroemulsie nie. Nietemin lei toevoeging van amiensoute, byvoorbeeld dietanolamiennitriet, tot verbeterde emulsifisering van die waterfase. 'n Toename in die alkohol (kosurfaktant) kettinglengte tot by oktanol verbeter ook die opname van die waterfase. Dus gee oktanol die beste resultate in terme van waterfase emulsifisering, veral by hoë sout konsentrasies. 'n Kerndoelwit was die bereiding van stabiele mikroemulsies met 'n hoë nitriet inhoud. Die maksimum mikroemulsies nitriet vlakke (uitgedruk as  $\text{NaNO}_2$  ekwivalente massa persentasie) wat bereik is was:

- Ongeveer 10% wanneer 'n 30%  $\text{NaNO}_2$  oplossing emulsifiseer is
- 23% as suiwer dietietanolamien nitriet (DEEAN) emulsifiseer is, en
- 23% vir mengsels van dietanolamien nitriet (DEtOHAN) en  $\text{NaNO}_2$  in water.

Die kationiese mikroemulsiesisteem was baseer op die dubbelketting kationiese surfaktant, didodesioldimetielammoniumchloried (DDAC). In hierdie geval is die emulsifisering van oplossings van die volgende asetaat soute bestudeer: ammonium, natrium, magnesium, sink en mangaan. Soos met die Atpol sisteem, is gevind dat 'n verhoging in die ioniese sterkte nadelig is vir die mikro-emulsifisering van groot volumes van die waterfase. In die DDAC sisteem lei 'n toename in die alkoholkettinglengte, verby butanol, tot verlaagde wateropname. Gevolglik bepaal die aard en konsentrasie van die surfaktant en kosurfaktant sowel as die ioniese sterkte van die waterfase die emulsiestabiliteit en emulsifiseringsgraad van die waterfase. In die algemeen bestaan daar 'n optimum ioniese sterkte waarby die soutkonsentrasie van die mikroemulsieformulasie maksimaal is.

## SLEUTELWOORDE

Surfaktant, water-in-olie mikroemulsies, didodesioldimetielammonium chloried, etoksileerde nonielfenol fosfaatester, amien, alkohol, ioniese sterkte.

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**CONTENTS**

|  | <b>Page</b> |
|--|-------------|
| ABSTRACT .....   | I           |
| OPSOMMING .....  | II          |
| ACKNOWLEDGEMENTS .....   | III         |
| NOMENCLATURE.....  | IX          |
| 1. INTRODUCTION.....   | 1           |
| 2. LITERATURE REVIEW.....  | 5           |
| 2.1 Definition and Role of Surfactants.....                        | 5           |
| 2.2 Properties of Surfactants .....                                | 5           |
| 2.3 Classifications of Surfactants .....                           | 6           |
| 2.3.1 Non-ionic surfactants .....                                  | 6           |
| 2.3.2 Anionic surfactants.....                                     | 7           |
| 2.3.3 Cationic surfactants .....                                   | 7           |
| 2.3.4 Amphoteric surfactants .....                                 | 7           |
| 2.4 Thermodynamics of the Adsorption of Surfactants .....          | 7           |
| 2.5 Micelles and Critical Micelle Concentration .....              | 11          |
| 2.5.1 Structure of micelles.....                                   | 11          |
| 2.5.2 Thermodynamics of micellisation.....                         | 12          |
| 2.5.3 Factors influencing the critical micelle concentration ..... | 13          |
| 2.6 Hydrophilic-Lipophilic Balance (HLB) of Surfactants.....       | 14          |
| 2.7 Emulsions .....  | 14          |
| 2.8 Microemulsions .....   | 17          |
| 2.8.1 Definition and discovery of microemulsions .....             | 17          |
| 2.8.2 Types of microemulsion.....                                  | 18          |
| 2.8.3 Properties of microemulsions.....                            | 18          |
| 2.8.4 Formulation and thermodynamics of microemulsions.....        | 19          |
| 2.8.5 Factors affecting the formation of microemulsions .....      | 21          |
| 2.8.6 Conductivity of microemulsions .....                         | 28          |
| 2.8.7 Microemulsion phase inversion .....                          | 29          |
| 2.8.8 Application of microemulsions .....                          | 30          |

|       |  |    |
|-------|--|----|
| 3.    | EXPERIMENTAL .....   | 32 |
| 3.1   | ATPOL 3205 system.....   | 32 |
| 3.2   | DDAC (Quat) system.....  | 32 |
| 3.3   | Preparation of the Amine Nitrite Salts .....   | 33 |
| 3.3.1 | Apparatus .....  | 33 |
| 3.3.2 | Planning.....  | 33 |
| 3.3.3 | Standard procedure for making amine nitrite salt .....   | 34 |
| 3.3.4 | Procedure for drying amine nitrite salts that are water soluble.....                                 | 34 |
| 3.3.5 | Procedure for testing miscibility with the oil phase.....  | 35 |
| 3.3.6 | Checking to ensure that amine nitrite salt has been formed.....                                      | 35 |
| 3.4   | Preparation of Microemulsions Containing Amine Nitrite .....   | 35 |
| 3.4.1 | Apparatus .....  | 35 |
| 3.4.2 | Titration of the surfactant.....   | 36 |
| 3.4.3 | Mixing of the samples .....  | 36 |
| 3.4.4 | Measurements.....  | 36 |
| 3.5   | Microemulsion Phase Ratios and Concentrations of Salts (ATPOL System) .....                          | 36 |
| 3.5.1 | Oil phase used .....   | 36 |
| 3.5.2 | Aqueous phase.....   | 37 |
| 3.5.3 | Preparation of the aqueous phase .....   | 37 |
| 4.    | RESULTS AND DISCUSSION .....   | 38 |
| 4.1   | Formation of w/o Microemulsion Containing Amine Nitrite Stabilised by ATPOL Surfactant .....         | 38 |
| 4.1.1 | Formation of amine nitrite.....  | 39 |
| 4.1.2 | Preparation of w/o microemulsion with amine nitrite.....   | 42 |
| 4.2   | Preparation of w/o microemulsion containing diethanolamine sulphate using the Atpol oil Phase .....  | 49 |
| 4.3   | Preparation of w/o microemulsion containing diethanolamine phosphate using the Atpol oil phase ..... | 52 |
| 4.4   | Preparation of w/o microemulsion stabilised by didodecyldimethyl ammonium chloride (DDAC).....       | 56 |
| 5.    | CONCLUSION .....   | 61 |
| 5.1   | Preparation of w/o microemulsion with amine nitrite stabilised by Atpol.....                         | 61 |

|      |   |    |
|------|---|----|
| 5.2  | Preparation of w/o microemulsion with diethanolamine sulphate and diethanolamine phosphate stabilised by Atpol..... | 62 |
| 5.3  | Preparation of w/o microemulsion with acetate salts using DDAC as surfactant....                                    | 62 |
| 5.4. | FINAL CONCLUSION .....  | 63 |
| 6.   | REFERENCES .....  | 64 |
| 7.   | APPENDIX: IONIC STRENGTH OF SALTS.....  | 68 |

## LIST OF FIGURES

|  | <b>Page</b> |
|--|-------------|
| Figure 2.1: Representation of an interface between bulk phases $\alpha$ and $\beta$ .....  | 8           |
| Figure 2.2: Surfactant monolayer coverage .....  | 10          |
| Figure 2.3: Critical micelle concentrations .....  | 10          |
| Figure 2.4: Schematic diagram of a water-in-oil (w/o) emulsion .....   | 15          |
| Figure 2.5: Formation and stability of an emulsion system .....  | 16          |
| Figure 2.6: Diagrammatic illustration of the formation of microemulsions .....   | 20          |
| Figure 4.1: Schematic representation of a water-in-oil microemulsion. Water droplets are dispersed in the main medium of oil .....           | 38          |
| Figure 4.2: Structure of an amine nitrite salt and the surfactant .....  | 39          |
| Figure 4.3: Mixing matrix for amine nitrite salts that can be used to make surfactants .....   | 42          |
| Figure 4.4: Viscosity of the microemulsion using oil phases I and X and different water phases .....   | 42          |
| Figure 4.5: Viscosity measurements of microemulsions with different oil phases containing a $\text{NaNO}_2$ water phase. ....                | 46          |
| Figure 4.6: Conductivity of microemulsions using oil phase I and different water phases .....  | 47          |
| Figure 4.7: Conductivity of microemulsions using different oil phases and a 40% $\text{NaNO}_2$ water phase.....                             | 47          |
| Figure 4.8: Effect of cosurfactant chain length on the maximum amounts of 4M aqueous diethanolamine sulphate emulsified by Atpol E3205 ..... | 50          |
| Figure 4.9: Microemulsion phase diagram: Emulsifying 4.0 M diethanolamine sulphate .....   | 50          |
| Figure 4.10: Microemulsion phase diagram: Emulsifying 2.0 M diethanolamine sulphate ....   | 51          |
| Figure 4.11: Microemulsion phase diagram: Emulsifying 1.0 M diethanolamine sulphate ....   | 51          |

|   |    |
|---|----|
| Figure 4.12: Maximum amounts of aqueous diethanolamine sulphate emulsified in a w/o microemulsion stabilised by Atpol E3205 .....           | 52 |
| Figure 4.13: Maximum amounts of aqueous diethanoldiethanolamine phosphate emulsified in a w/o microemulsion stabilised by Atpol E3205 ..... | 54 |
| Figure 4.14: Microemulsion phase diagram: Emulsifying 4 M diethanoldiethanolamine phosphate.....  | 55 |
| Figure 4.15: Microemulsion phase diagram: Emulsifying 1 M diethanoldiethanolamine phosphate.....  | 56 |
| Figure 4.16: Aqueous phase solubilization by w/o microemulsion containing ammonium acetate with different cosurfactants.....                | 58 |
| Figure 4.17: Maximum amounts of sodium acetate solubilization by the DDAC w/o microemulsion with different cosurfactants.....               | 59 |
| Figure 4.18: Maximum amounts of magnesium acetate solubilization by the DDAC w/o microemulsion with different cosurfactants.....            | 60 |
| Figure 4.19: Effects of salinity and cosurfactant in the w/o microemulsion stabilised by DDAC, with zinc acetate as the aqueous phase ..... | 60 |

## LIST OF TABLES

|   | <b>Page</b> |
|---|-------------|
| Table 2.1: Properties of emulsions and microemulsions.....  | 18          |
| Table 4.1: Results of the yield calculation for di-isobutyl amine nitrite salt .....  | 39          |
| Table 4.3: Amine nitrite salt mixtures tested .....   | 41          |
| Table 4.4: The different oil phases used .....  | 44          |
| Table 4.5: Amounts of sodium hydroxide/diethanolamine needed for the different surfactants .....                                  | 45          |
| Table 4.6: Samples mixed with amine nitrite salts as water phase .....  | 48          |
| Table 4.7: Maximum percentages of NaNO <sub>2</sub> achieved in the experiments .....   | 48          |
| Table 4.8: Maximum amounts of aqueous phase solubilized in microemulsion for diethanolamine sulphate.....                         | 49          |
| Table 4.9: Maximum amounts of aqueous phase in microemulsion for diethanolamine phosphate.....                                    | 53          |
| Table 4.10: Maximum amounts of aqueous phase in the microemulsion containing ammonium acetate and the oil phase with butanol..... | 57          |

|   |    |
|---|----|
| Table 4.11: Effect of substituting butanol with hexanol in the ammonium acetate w/o microemulsion stabilised by DDAC .....      | 57 |
| Table 4.12: Solubilization of sodium acetate in the DDAC system with butanol .....  | 58 |
| Table 4.13: Amounts of sodium acetate in the w/o microemulsion at different concentrations with hexanol as a cosurfactant ..... | 59 |

## LIST OF SCHEMES

|  | <b>Page</b> |
|--|-------------|
| Scheme 1: Reaction of secondary amine with nitrite ion to form amine nitrite salt..... | 34          |

## NOMENCLATURE

| <b>SYMBOL</b> | <b>ABBREVIATION</b>                                |
|---------------|--|
| ATPOL         | Nonylphenol ethoxylated phosphate ester surfactant |
| c.m.c.        | Critical micelle concentration                     |
| CTAB          | Cetyltrimethylammonium bromide                     |
| DBA           | Dibutyl amine                                      |
| DDAC          | Didodecyldimethyl ammonium chloride                |
| DIBA          | Diisobutyl amine                                   |
| DIBAN         | Diisobutyl amine nitrite                           |
| DEEA          | Diethyl ethanol amine                              |
| DEEAN         | Diethyl ethanol amine nitrite                      |
| DEtOHA        | Diethanolamine                                     |
| DEtOHAN       | Diethanolamine nitrite                             |
| DICHA         | Dicyclohexyl amine                                 |
| DHA           | Dihexyl amine                                      |
| EDCA          | Ethyl dicyclohexyl amine                           |
| EP            | Ethanolpiperidine                                  |
| SDS           | Sodium dodecyl sulphate                            |
| TBA           | Tributyl amine                                     |
| g             | Grams  |
| M             | Molarity mol/L                                     |
| nm            | Nanometre  |
| o/w           | Oil-in-water                                       |
| Quat          | Cationic surfactant (DDAC)                         |
| s             | Second   |
| w/o           | Water-in-oil                                       |

## 1. INTRODUCTION

Research and technology are recognized globally as a source of economic growth for every country. It is through research that South Africa is able to compete globally in terms of producing new products and raw materials to sustain its industries. Most of the raw materials used in our industries and products are imported from overseas. The challenge facing product development today is to keep up with the rapid changes and continuous improvements in existing products. We therefore need to come up with means of enhancing our products, for instance by using alternative lower-cost raw materials or by coming up with new processes for making products. For instance, wax emulsions for floor polishes are sourced from many raw material waxes, some of which are imported from overseas.

According to Attwood and Florence (1983), emulsions traditionally prepared with naturally occurring gums such as acacia and tragacanth have been used in pharmacy for centuries as means of administering oils or vitamins. Concentrated emulsions are used in topical therapy, such as in semi-solid vehicles (ointments). The replacement of natural gums with surfactants has led to the advantage of a more rigorous fundamental approach to the formulation of different systems. The presence of surfactant micelles in a system leads to the potential solubilization of components such as preservatives, flavours and drugs. There is increasing demand to reduce the cost of pharmaceutical products, cosmetics and household products. Some of these products are basically made from expensive ingredients solubilized in water or oil and stabilized by surfactants. For instance, body lotions and floor polishes are made from oil, water, surfactants, perfumes and colorants.

Such a system consisting of oil and water phases is scientifically referred to as an *emulsion*. An emulsion is a product made from two immiscible liquids stabilized by a surfactant. The surfactant helps to reduce the surface tension between the oil phase and water phase. If the water is dispersed in the oil, the system is referred to as a water-in-oil (w/o) emulsion, and if the oil is dispersed in the water, the system is referred to as an oil-in-water (o/w) emulsion. Generally, emulsions are opaque in appearance.

Whether the emulsion will be w/o or o/w depends on the nature of the surfactant used and other factors that are discussed later in the literature survey. Emulsion systems are generally unstable, i.e. they separate over a certain period. The manufacture of emulsions generally

involves the application of external energy, such as heating and vigorous stirring. The large amount of energy applied is further required to break up the particles of the dispersed phase into smaller droplets. Many scientists have studied the behaviour of emulsions and how to enhance their stability. One way of enhancing the stability of an emulsion is by reducing the droplet size of the dispersed phase. This can be done by increasing the processing/stirring time or adding more surfactant to the system. However, both options have time and cost implications.

In the early 1940s, Schulman added an alcohol to an emulsion system and the system turned from opaque to transparent. He discovered that the transparency of the emulsion was due to the decreased droplet size of the dispersed phase to about 10 nm. This is because the alcohol partitions itself between the surfactant molecules, thereby further reducing the surface tension to below zero. Hence microemulsions do not require external energy during their manufacture. He then named the system *microemulsion*. Since then, scientists have studied the phase behaviour of these systems. Microemulsions are now widely applied and in the chemical industry, particularly in the cosmetics, pharmaceutical and oil industries. Most household and cosmetic products in everyday use, e.g. personal care products, slimming products, etc. are either microemulsions or emulsions. Microemulsion products are often preferred in the chemical industry because they are indefinitely stable and are easy to process. They are manufactured through a cold process of gentle stirring.

Many active ingredients in cosmetic and pharmaceutical products are expensive and may even be harmful if used in large quantities. In most cases, low dosage levels of the active ingredients suffice. It is therefore convenient to solubilize them in large quantities of an inert diluent (e.g. water) in the form of a microemulsion. The formation of microemulsions requires four components in appropriate ratios, i.e. oil phase, water phase, surfactant and cosurfactant (the latter is usually a short-chain alcohol).

Just as in emulsions, in microemulsions the water phase can be dispersed in a continuous oil phase. Such a system is called water-in-oil (w/o) microemulsion and is applicable where an oily product is desired (De Castro Dantas *et al.*, 2001). When the oil is dispersed in a continuous aqueous phase, the system is referred to as an oil-in-water (o/w) microemulsion. The type of microemulsion that is formed depends on the chemical nature of the surfactant and the ratio between the oil and aqueous phases. The increased solubility of organic

materials in aqueous surfactant solutions is a phenomenon that has found application in many scientific and technological areas. It is only recently that a good understanding of the structural requirements for optimum solubilization has begun to develop as a result of extensive experimental and theoretical work. Empiricism is slowly giving way to well-thought-out correlations between the requirements of a system and the chemical structure of the surfactant that will provide the necessary environment to promote the solubilization process. Solubilization is defined as “the preparation of a thermodynamically stable, isotropic solution of a substance normally insoluble or only slightly soluble in a given solvent by the addition of one or more amphiphilic compounds at or above their critical micelle concentration” (Meyers, 1992).

The oil phase is usually the most expensive portion of an emulsion or microemulsion. In some applications it is necessary to reduce the quantity of the oil phase in the microemulsion formulation. This dissertation focuses on such a system in which the optimization of the microemulsion required the minimization of the oil phase content of an oil continuous system. In addition, the requirement was to maximize the salt content (dissolved in the aqueous phase) of the formulation. This was done by investigating aqueous phases of different ionic strengths and determining the optimum ionic strength at which the maximum quantity of the aqueous phase is solubilized in the microemulsion. The effect of the cosurfactant on the microemulsion formulation was also investigated. The investigation was done for only two microemulsion systems. The first microemulsion system was stabilized by an anionic surfactant –nonyl phenol ethoxylated phosphate ester – and the second one was stabilized by a cationic surfactant – didodecylammonium chloride.

The project focused on the effect of ionic strength and cosurfactants on the formulation of w/o microemulsion systems. The objective of the study was to determine the effects of salinity (ionic strength), the cosurfactant (in this case butanol) and surfactant type on formulation of w/o microemulsions. To achieve the above objective, it is desired that this w/o microemulsion system should:

- ❑ Contain a minimal amount of surfactant (emulsifier) and organic components (oil)
- ❑ Contain a high concentration of salt solution.

To achieve this, we need to maximise the amount of the aqueous phase solubilized in the microemulsion. The microemulsions under investigation consisted of the following components:

- i. Surfactant (nonylphenol ethoxylated phosphate ester) (ATPOL system) and Quat surfactant (didodecyldimethyl ammonium chloride) (DDAC system)
- ii. Cosurfactant (butanol/hexanol/octanol)
- iii. Oil (Shellsol 2325, mixture of paraffins, cycloparaffins and aromatics)
- iv. Water (saline solution).

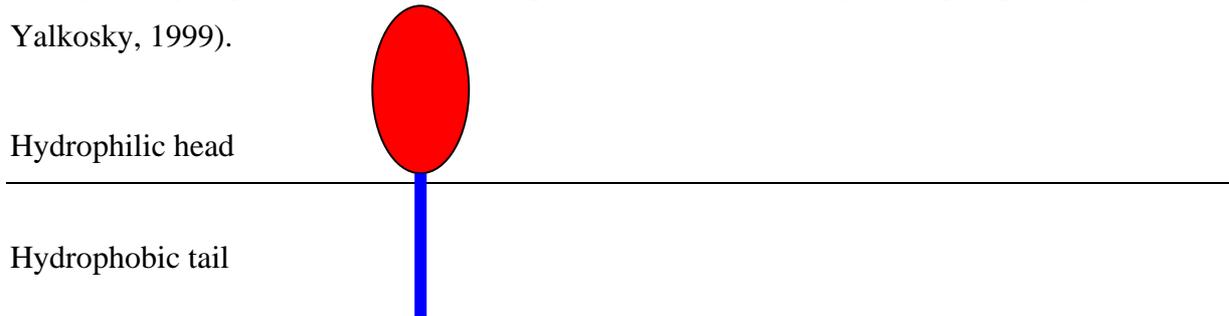
Other aspects were also studied to determine the effect on microemulsion formulation (see below). In addition, the effect of ionic strength on the formation of w/o microemulsions was studied.

1. Microemulsion systems containing different diethanolamine salts were studied for the ATPOL system. The following diethanolamine salts were used to determine the effect of ionic strength on the microemulsion formulation:
  - Diethanolamine nitrite salt
  - Diethanolamine sulphate salt
  - Diethanolamine phosphate salt.
2. Microemulsion systems containing different acetate salts were studied for the DDAC system. The following salts were used in the aqueous phase to determine the effect of ionic strength on the microemulsion formulation:
  - Ammonium acetate
  - Sodium acetate
  - Magnesium acetate
  - Zinc acetate.

## 2. LITERATURE REVIEW

### 2.1 Definition and Role of Surfactants

A surfactant is a molecule that is soluble in both oil and water phases. This is because surfactants contain both a water-miscible group and an oil-miscible group. They are often referred to as “schizophrenic molecules”. The water-miscible part of a surfactant is called the *hydrophilic* group and the oil-miscible part is called the *hydrophobic* group (Meyers, 1992; Yalkosky, 1999).



The hydrophobic tail is mainly a series of  $\text{CH}_2$  groups, which are non-polar, whereas the hydrophilic groups are polar molecules. The nature of the hydrophobic groups may be significantly more varied than that of the hydrophilic groups. Quite often they are long-chain hydrocarbon radicals; however, they may include groups such as:

1. Long, straight-chain alkyl groups
2. Branched-chain alkyl groups
3. Alkylbenzenes
4. Alkyl naphthalenes
5. Fluoroalkyl groups
6. Polydimethylsiloxanes
7. High-molecular-weight polyoxypropylene glycol derivatives
8. Rosin derivatives
9. Miscellaneous structures, depending on the creativity of the synthetic chemist (Meyers, 1992).

### 2.2 Properties of Surfactants

Surfactants can be employed in many industrial applications such as:

- ❑ Detergent or cleaning applications (e.g. soaps)
- ❑ Wetting

- Foaming and defoaming
- Emulsifications and demulsifications
- Solubilization
- Dispersions.

Each application requires specific chemical orientation of the surfactant. Surfactants have been classified into categories due to their chemical nature.

### **2.3 Classifications of Surfactants**

The hydrophilic part of the most effective soluble surfactants is often an ionic group. Ions have a strong affinity for water owing to their electrostatic attraction to the water dipoles and are capable of pulling a fairly long hydrocarbon into the solution with them. For instance, palmitic acid, which is virtually unionised, is insoluble in water whereas sodium palmitate, which is almost completely ionised, is soluble in water.

It is also possible to have non-ionic hydrophilic groups, which also exhibit a strong affinity for water; for example the monomer units of a poly (ethylene oxide) chain each show a modest affinity. Surfactants are classified as anionic, cationic, non-ionic or ampholytic according to the charge carried by the surface-active part of the molecule (Meyers, 1992; Yalkosky, 1999). In addition, surfactants are often named in relation to their technological application; hence names such as detergent, wetting agent, emulsifier and dispersant.

#### **2.3.1 Non-ionic surfactants**

Non-ionic surfactants do not contain a charge on the hydrophilic head. An example of a non-ionic surfactant is alkyl dialkanolamide. It is a good wetting agent and solubilizer. An advantage enjoyed by the non-ionics is that the lengths of both the hydrophilic and hydrophobic groups can be varied. Two of the most important features of non-ionic systems are as follows:

- They can accommodate brines of salinity much higher than can classic ionic systems.
- The soft interactions between polar groups are relatively sensitive to any change in temperature – hence the delicate force balance that presides over the existence of the

structures, and phase diagrams whose outlook may be markedly temperature-dependent.

### **2.3.2 Anionic surfactants**

Anionic surfactants contain a negative charge on the hydrophilic head. An example of an anionic surfactant is alkyl sulphonate. Anionics are good emulsifiers as well as foaming agents and are therefore applicable in detergents. They are the most widely used surfactants on account of their cost and performance.

### **2.3.3 Cationic surfactants**

Cationic surfactants contain a positive charge on the hydrophilic head group. They have biocidal/germicidal activity and conditioning properties. Examples of cationic surfactants are quaternary amines.

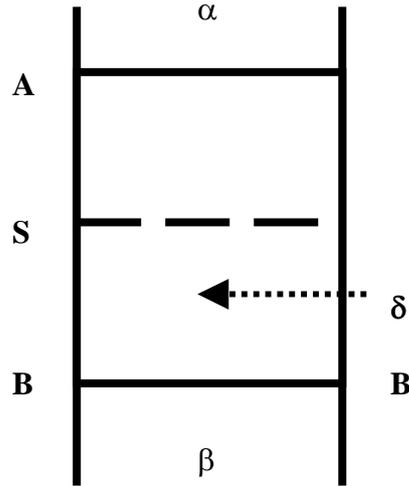
### **2.3.4 Amphoteric surfactants**

Amphoterics have both negative and positive charges on the hydrophilic group. They can be used as foam boosters, conditioners, emulsifiers, dispersing agents and thickeners, and are stable over a wide range of pH. An example of an Amphoteric is amine betaine.

## **2.4 Thermodynamics of the Adsorption of Surfactants**

The Gibbs adsorption equation enables the extent of adsorption at a liquid surface to be estimated from surface tension data. It is convenient to regard the interface between two phases as a mathematical plane, such as SS in Figure 2.1 below.

This approach is, however, unrealistic, especially if an adsorbed film is present. Not only will such a film itself have a certain thickness, but also its presence may influence nearby structures and result in an interfacial region of varying composition with an appreciable thickness in terms of molecular dimensions. If a mathematical plane is taken to represent the interface between two phases, adsorption can be described conveniently in terms of surface excess concentration.



**Figure 2.1: Representation of an interface between bulk phases  $\alpha$  and  $\beta$**

If  $n_i^r$  is the amount of component  $i$  in the surface phase  $\delta$  (Figure 2.1) in excess of that which would have been in  $\delta$  had the bulk phases  $\alpha$  and  $\beta$  extended to a surface  $SS$  with unchanging composition, the surface excess concentration of component  $i$  is given by:

$$\Gamma_1 = n_1^\delta / A \quad (1)$$

where  $A$  is the interfacial area.  $\Gamma_1$  may be positive or negative, and its magnitude depends on the location of  $SS$ , which must be chosen arbitrarily. The total thermodynamic energy of the system is given by the expression

$$U = TS - pV + \sum \mu_i n_i \quad (2)$$

The corresponding expression for the thermodynamic energy of a surface phase is:

$$U^\delta = TS^\delta - pV^\delta + \gamma A + \sum \mu_i n_i^\delta \quad (3)$$

Differentiating Equation (3)

$$dU^\delta = TdS^\delta + S^\delta dT - pdV^\delta - V^\delta dp + \gamma dA + Ad\gamma + \sum \mu_i dn_i^\delta + \sum n_i^\delta d\mu_i \quad (4)$$

From the first and second laws of thermodynamics:

$$dU = TdS - pdV + \sum \mu_i dn_i \quad (5)$$

or for a surface phase:

$$dU^\delta = TdS^\delta - pdV^\delta + \gamma dA + \sum \mu_i dn_i^\delta \quad (6)$$

Subtracting Equation (6) from (4):

$$S^\delta dT - pdV^\delta + Ad\gamma + \sum n_i^\delta d\mu_i = 0 \quad (7)$$

Therefore at constant pressure and temperature:

$$d\gamma = -\sum n_i^\delta d\mu_i / A = -\sum \Gamma_i d\mu_i \quad (8)$$

For a simple two-component solution (consisting of a solvent and a solute), Equation (8)

becomes 
$$d\gamma = -\Gamma_A d\mu_A - \Gamma_B d\mu_B \quad (9)$$

A convenient choice of location of this surface for a binary solution is that at which the surface excess concentration of the solvent ( $\Gamma_A$ ) is zero. The above expression then simplifies to:

$$d\gamma = -\Gamma_B d\mu_B \quad (10)$$

Since chemical potential changes are related to activities by:

$$\mu_B = \mu_B^\delta + RT \ln a_B \quad (11)$$

then 
$$d\mu_B = RT d \ln a_B \quad (12)$$

Therefore

$$\Gamma_B = -(1/RT)(d\gamma / d \ln a_B) = -(a_B / RT)(d\gamma / da_B) \quad (13)$$

or for dilute solutions,

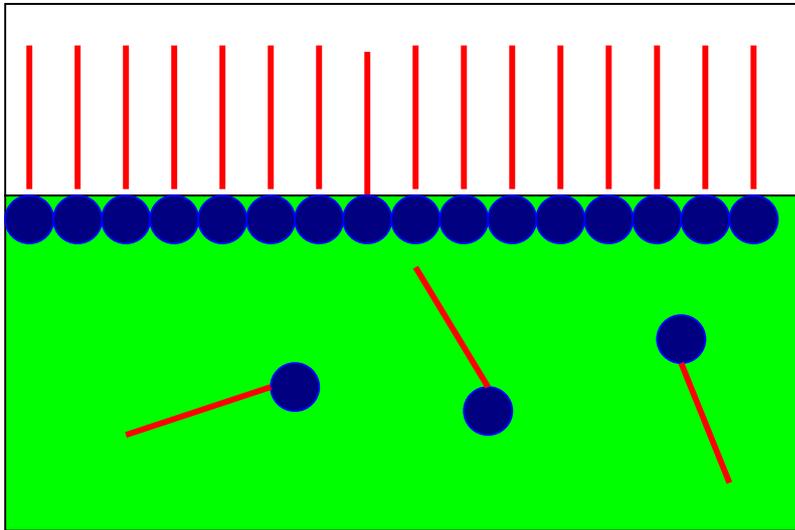
$$\Gamma_B = -(c_B / RT)(d\gamma / dc_B) \quad (14)$$

which is the form in which the Gibbs equation is usually quoted.

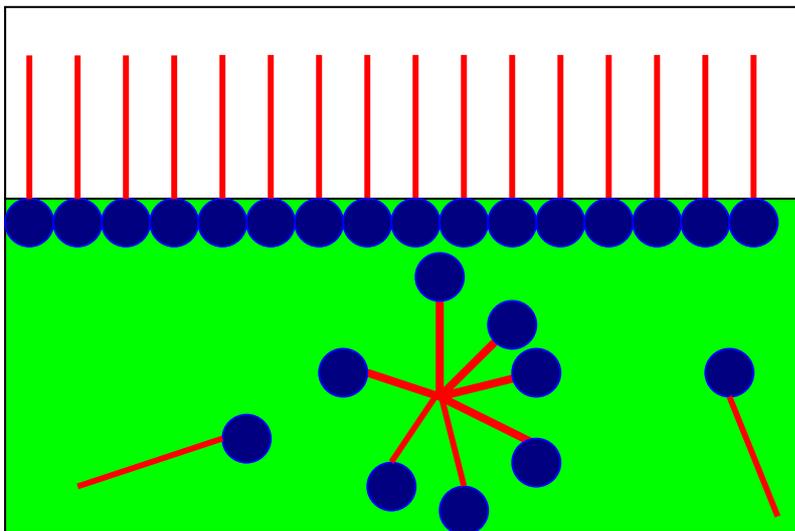
The Gibbs equation in this form could be applied to a solution of a non-ionic surfactant. For a solution of a 1:1 ionic surfactant, a factor of 2 is required to allow for the simultaneous adsorption of both cations and anions, and Equation (14) will be modified to:

$$\Gamma_B = -(c_B / 2RT)(d\gamma / dc_B) \quad (15)$$

In the presence of excess electrolyte, however, an electrical shielding effect will operate and Equation (14) will be applied (Everett, 1994).



**Figure 2.2: Surfactant monolayer coverage**



**Figure 2.3: Critical micelle concentrations**

## 2.5 Micelles and Critical Micelle Concentration

When a small amount of surfactant is added to the bulk of a system, the water will solubilize and disperse it. As more surfactant is added to the system, the system will become saturated with surfactant. Further addition of surfactant will start to form micelles (see Figure 2.3) (Bennet *et al.*, 1968). A micelle is a small aggregation of surfactant molecules in the system. These molecules of surfactant are oriented with the lipophilic end of the surfactant towards the oil phase and the hydrophilic end towards the aqueous phase (see Figure 2.2). Solutions of highly surface-active materials exhibit unusual physical properties. In dilute solutions the surfactant acts as a normal solute. At fairly well defined concentrations, however, abrupt changes in several physical properties, such as turbidity, electrical conductivity and surface tension, take place.

It has been pointed out that this seemingly anomalous behaviour could be explained in terms of the micelles of the surfactant ions, in which the lipophilic hydrocarbon chains are orientated towards the interior of the micelles, leaving the hydrophilic groups in contact with the aqueous medium. The concentration above which micelle formation becomes appreciable is termed the *critical micelle concentration* (c.m.c.). Micellisation is therefore an alternative mechanism to adsorption by which the interfacial energy of a surfactant solution may decrease. The c.m.c. can be determined by measuring any micelle-influenced physical property as a function of surfactant concentration. In practice, surface tension, electrical conductivity and solubilization measurements are the most popular. The choice of physical property will have a slight influence, as will the procedure adopted to determine the point of discontinuity.

### 2.5.1 Structure of micelles

Possible micelle structures include spherical, laminar and cylindrical arrangements. Micelles tend to be approximately spherical over a fair range of concentrations above the c.m.c. but there are often marked transitions to larger, non-spherical liquid crystals structures at high concentrations. Systems containing spherical micelles tend to have low viscosities.

The free energies between micellar phases tend to be small and consequently the phase diagrams for these systems tend to be quite complicated and sensitive to additives. Some of the experimental evidence favouring the existence of spherical, liquid-like micelles is summarised as follows:

1. Critical micelle concentration and the size of the micelle depend mostly on the nature of the lyophobic part of the surfactant.
2. The number of molecules in a micelle of a given surfactant shows a very narrow distribution.
3. The length of the surfactant's hydrocarbon chain will dictate the radius of a spherical micelle. This in turn determines the spacing of the outer polar groups. For example, a dodecyl sulphate group would be expected to consist of approximately one-third sulphate groups and two-thirds hydrocarbons (Everett, 1994; Myers, 1992; Shaw, 1994; Vold and Vold, 1983).

### 2.5.2 Thermodynamics of micellisation

There is a theory relating to the abruptness with which micellisation takes place above a certain critical concentration. The theory applies to the law of mass action towards the attainment of equilibrium between non-associated molecules and ions and micelles, as illustrated by the following calculation for the micellisation of non-ionic surfactants (Everett, 1994; Myers, 1992; Shaw, 1994; Vold and Vold, 1983). If  $c$  is the stoichiometric concentration of the solution,  $x$  is the fraction of monomer units in aggregation and  $m$  is the number of monomer units per micelle, and applying the law of mass action:

$$K = (cx/m)/[c(1-x)]^m \quad (16)$$

For a moderately large value of  $m$ , this expression requires that  $x$  should remain very small up to a certain value of  $c$  and increase rapidly thereafter. Since the equilibrium constant,  $K$ , in Equation (16) and the standard free energy change,  $\Delta G^\theta$ , for the micellisation of 1 mole of surfactant are related by

$$\Delta G^\theta = -(RT/m)\ln K \quad (17)$$

Substituting equation (16) into Equation (17) yields

$$\Delta G^\theta = -(RT/m)\ln(cx/m) + RT\ln[c(1-x)] \quad (18)$$

At the c.m.c.,  $x = 0$  and

$$G^{\theta} = -RT \ln(\text{c.m.c.}) \quad (19)$$

Therefore,  $\Delta S^{\theta} = -d(\Delta G^{\theta})/dT$

$$= -(RT)[(d \ln(\text{c.m.c.})/dT)] - R \ln(\text{c.m.c.}) \quad (20)$$

and  $\Delta H^{\theta} = \Delta G^{\theta} + T\Delta S^{\theta}$

$$= -RT^2[d \ln(\text{c.m.c.})/dT] \quad (21)$$

In general, micellisation is an exothermic process and the c.m.c. increases with increasing temperature.

This is, however, not universally the case; for example, the c.m.c. of sodium dodecyl sulphate in water shows a shallow minimum between about 20 °C and 25 °C. At lower temperatures, the enthalpy of micellisation given by Equation (21) is positive (endothermic), and micellisation is entirely entropy-directed (Everett, 1994; Attwood and Florence, 1983).

### 2.5.3 Factors influencing the critical micelle concentration

- Increasing the hydrophobic part of the surfactant molecules favours micelle formation. In an aqueous medium, the c.m.c. of an ionic surfactant is approximately halved by the addition of each CH<sub>2</sub> group. For non-ionic surfactants, this effect is even more pronounced. This trend usually continues up to about the C<sub>16</sub> member. Above the C<sub>18</sub> member, the c.m.c. tends to be approximately constant (Everett, 1994).
- With ionic micelles, the addition of simple electrolytes reduces the repulsion between the charged groups at the surface of the micelle by the screening action of the added ions. The c.m.c. is therefore lowered.
- The addition of organic molecules can affect the c.m.c. in a variety of ways. The most pronounced changes are effected by those molecules (medium chain-length alcohols) that can be incorporated into the outer regions of the micelle. There they can reduce electrostatic repulsion and steric hindrance, thus lowering the c.m.c. Micelles

containing more than one surfactant often form readily with a c.m.c. lower than any of the c.m.c.'s of the pure constituents (Attwood and Florence, 1983).

## 2.6 Hydrophilic-Lipophilic Balance (HLB) of Surfactants

Becher introduced the concept of HLB in order to characterise the potential relative solubility of a surfactant in water and in oil (Becher, 1984 in Friberg and Bothorel, 1987). The empirical definition proposed for ethoxylated non-ionic surfactants has proved particularly valuable in the formulation of emulsions:

$$\text{HLB} = 20M_{\text{H}} / (M_{\text{L}} + M_{\text{H}}) \quad (22)$$

where  $M_{\text{H}}$  and  $M_{\text{L}}$  are the molecular weights of the hydrophilic moieties. According to Friberg and Bothorel, there is no reason to believe that the HLB is a universal parameter for any property of an oil and/or water surfactant mixture.

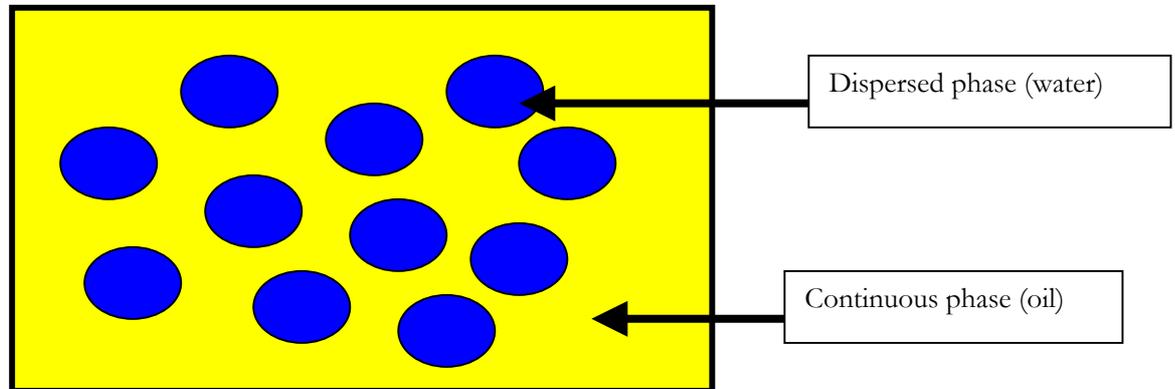
According to Equation (22) applied to hydrogenated polyoxyethylene alcohols, the HLB remains constant if the addition of one oxyethylene group is counterbalanced by an increase in the hydrocarbon chain by three methylene groups. Surfactants with a low HLB (below 7) are more soluble in oil and those with an HLB above 12 are more soluble in water (Leon, 1977).

## 2.7 Emulsions

The term *emulsion* usually refers to a dispersed system of two or more immiscible liquids (such as oil and water) in which one liquid in the form of droplets is homogeneously dispersed in another one (Everett, 1977; Becker, 1966; Shahidzadeh *et al.*, 1999; Wennerstrom *et al.*, 1997). Since such a dispersed system often appears milky, the term emulsion is adopted. Emulsions are of two distinct types: a dispersion of fine oil droplets in an aqueous medium, called an oil-in-water (o/w) emulsion, or one of aqueous droplets in oil, called water-in-oil (w/o) emulsion (see Figure 2.4).

The type of emulsion formed depends on a number of factors. If the ratio of the amounts of the two phases is very low, the phase present in small amounts is often the dispersed phase; if

the phase volumes are roughly equal, other factors such as surfactant type determine which type of emulsion is formed. However, this is not always the case.



**Figure 2.4: Schematic diagram of a water-in-oil (w/o) emulsion**

It is usually possible to determine the type of emulsion by examining the effect of diluting it with one of the phases. A w/o emulsion is miscible with oil and an o/w is miscible with water. For instance, milk may be diluted with water, which shows that it is an o/w emulsion, whereas mayonnaise, a w/o emulsion, can be diluted with oil.

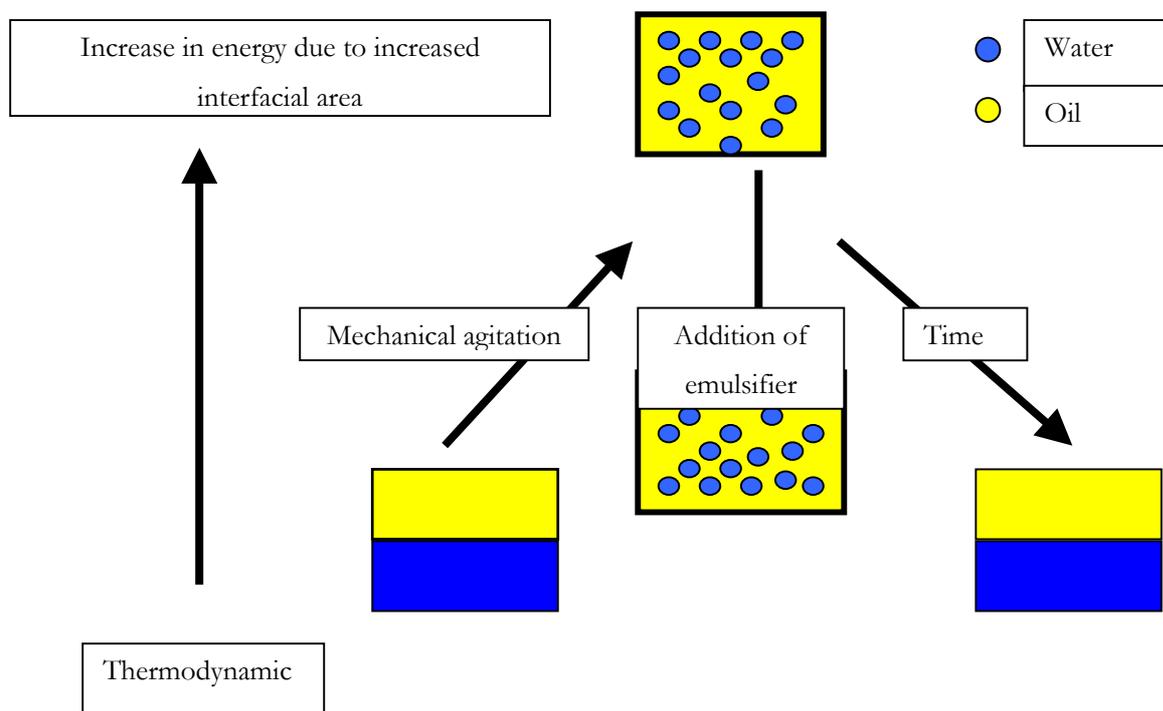
There are also emulsions that are called *multiple emulsions* (Taelman and Loll, 1994). Multiple emulsions are complex systems that can be considered as emulsions of emulsions. They are formed from a dispersion of droplets which themselves contain smaller droplets of a liquid identical, or similar, to the external continuous phase.

### **2.7.1 Thermodynamics and formation of emulsions**

The formation of emulsions by breaking down one liquid in the presence of another may be achieved by mechanical means. In some instances simple shaking or stirring may be sufficient; in others it is necessary to apply very strong hydrodynamic forces, as is done in colloidal mills. The success of an emulsifying process depends largely on the interfacial tension between the two liquids. This can be modified by the addition of an appropriate emulsifying agent.

In favourable cases, where the interfacial tension is very low, the energy needed to form an emulsion is correspondingly small and may be provided by the thermal motion of the molecules. The formation of emulsions, which involves an increase in the interfacial area between the two phases, is accompanied by an increase in free energy. The ease of formation of an emulsion may be measured by the amount of work needed for its formation: the lower the interfacial tension, the less work is needed and the more readily the emulsion is formed. The addition of emulsifying agents (surfactants), which adsorb at the interface and lower the interfacial tension, is therefore usually necessary if a stable emulsion is to be formed (Everett, 1994).

The ease of formation of an emulsion increases and the droplet size achievable decreases as the interfacial tension decreases. Systems in which the interfacial tension falls to near zero may emulsify spontaneously under the influence of thermal energy and produce droplets so small (<10 nm) that they scatter light and give rise to clear dispersions. Such emulsions are called *microemulsions*. They are effectively monodisperse and are thermodynamically stable. Figure 2.5 below illustrates the formation of an emulsion.



**Figure 2.5: Formation and stability of an emulsion system**

## 2.8 Microemulsions

Microemulsions are transparent vesicles containing large amounts of both water and hydrocarbons. They are colloiddally dispersed systems and hence show an essential distinction from molecular solutions of hydrocarbons and water (Friberg and Bothorel; 1987, Miguel *et al.*, 2001; Attwood and Florence, 1983). The latter kind may be exemplified by the system of water, benzene and isopropanol. In a microemulsion, the hydrocarbon/water colloidal solution is commonly stabilised by a combination of a surfactant and a medium-chain-length alcohol, such as pentanol. Microemulsions have found a great variety of uses and they are not only scientifically but also technologically well established. According to Friberg and Bothorel (1987), microemulsions are at present the focus of extensive research efforts. However their definition is open to debate.

### 2.8.1 Definition and discovery of microemulsions

Schulman and Hoar first proposed the term microemulsions in the 1940s. They discovered that titration of an opaque emulsion with a medium-chain alcohol, such as hexanol produced a transparent system. The additional component, alcohol, was termed a *cosurfactant*. Further study confirmed that such transparent emulsions had dispersed-phase particles smaller than 0.1  $\mu\text{m}$  (Prince, 1977). The term microemulsion was thus coined. Microemulsions are currently the subject of investigations because of their wide range of potential and actual utilisation in enhanced oil recovery (Everett, 1994; Friberg and Bothorel, 1987). Most of the investigations performed on microemulsions deal with aspects such as stability, phase diagrams, structure and interactions.

Microemulsions are composed of two mutually immiscible liquid phases, one spontaneously dispersed in the other, with the assistance of one or more surfactants. They are generally ternary fluid systems made up of an aqueous phase, an oil phase, a surfactant and a cosurfactant (Friberg and Bothorel, 1987; Leon, 1977; Fernandez *et al.*, 1999; Meyers, 1992; Garcia-Sanchez *et al.*, 2001). The resulting system is composed of micro droplets or swollen micelles, consisting of an oily or aqueous centre surrounded by a mixed film of surfactant and cosurfactant.

Microemulsions are defined as thermodynamically stable dispersions stabilised by surfactant molecules, whose particle size in the dispersed phase is between 10 and 100 nm (Miguel *et al.*, 2001; Chunsheng *et al.*, 2000; Leon, 1977; Hamid and Vera, 1996; Jihu and Romsted, 1997; Mehta and Bala, 2000; Fernandez *et al.*, 1999; Panayiotis and Scalart, 1997; Wolfgang, 1995; Alany *et al.*, 2000; Schulman in Eriksson *et al.*, 2004; Goncalves *et al.*, 2003; Binks *et al.*, 2003).

### 2.8.2 Types of microemulsion

The microscopic structure of the microemulsion depends on the volume fraction of the dispersed phase, and on the temperature and chemical properties of its components. Like emulsions, microemulsions are of the w/o and o/w types and invert from one type to the other through a change in the type of emulsifier (Leon, 1977). The distinction between emulsions and microemulsions is fairly clear. The droplet size of the dispersed phase in an emulsion is greater than 200 nm, meaning such systems are opaque. Microemulsions, however, normally have a droplet diameter of 100 nm or less. Because those particles are much smaller than the wavelength of visible light, they are normally transparent (Meyers, 1992).

### 2.8.3 Properties of microemulsions

The properties of microemulsions and emulsions are shown in Table 2.1 below.

**Table 2.1: Properties of emulsions and microemulsions**

| Property             | Emulsion   | Microemulsion   |
|----------------------|--|---|
| Dispersity           | Particle >0.1 $\mu\text{m}$ ; visible under microscope             | Particles are usually 0.01-0.1 $\mu\text{m}$ . Invisible under microscope |
| Light transmittance  | Non-transparent  | Transparent   |
| Stability            | Non-stable, can be stratified by centrifuge                        | Thermodynamically stable; cannot be stratified by centrifuge              |
| Amount of surfactant | Small addition of surfactants; cosurfactant not necessary          | Larger amounts of surfactants and cosurfactants are necessary             |
| Miscibility          | O/w type is immiscible with oil; w/o type is immiscible with water | Miscible with oil and water within some limits                            |

#### 2.8.4 Formulation and thermodynamics of microemulsions

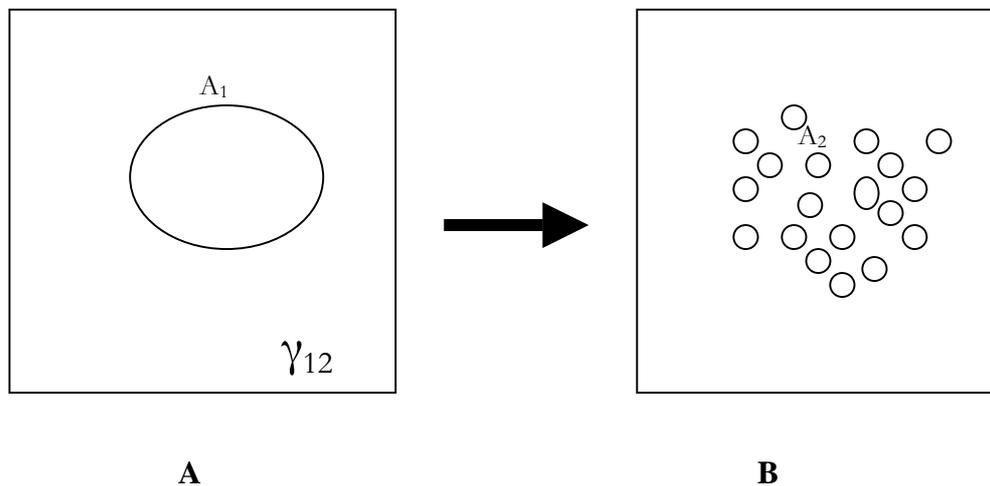
The formation of a microemulsion involves the creation of a situation in which the oil-water interfacial tension approaches zero (Ruckenstein, 1998). With most single ionic surfactants and single non-ionic surfactants this is not possible, since  $\gamma_{ow}$  is still sizeable when above c.m.c. when the limit of solubility is reached. To achieve the required lowering of  $\gamma_{ow}$  a cosurfactant must be included.

In view of the high oil-water interfacial area that must be created, the fraction of the emulsifying agent in the microemulsion formulation tends to be significantly higher than that in an ordinary emulsion. With  $\gamma_{ow}$  close to zero, a microemulsion will form spontaneously and hence they are thermodynamically stable. Studies show that in microemulsion systems the interfacial tension between water and oil is too low to be measured. This is undoubtedly the reason for the high stability of such systems since they are thermodynamically stable. This means that during long-term storage, microemulsions exhibit no demulsification and cannot be stratified by a centrifuge. Thus, centrifugation can be used to distinguish between microemulsions and emulsions.

The driving force behind the formation of microemulsions is the low interfacial energy and high entropy. The interfacial area is reduced by the presence of surfactants and cosurfactants. Surface-active materials (surfactants) consist of molecules containing both polar and non-polar parts. The tendency of surfactants to pack into an interface favours the expansion of the interface; this must therefore be balanced against the tendency for the interface to contract under normal surface tension. If  $\pi$  is the expanding pressure of an adsorbed layer of surfactant ( $\gamma$ ), then the surface tension will be lowered to a value  $\gamma = \gamma_0 - \pi$ ; here  $\gamma_0$  is the interfacial area of a clean surface (Leon, 1977).

$\pi_0$  and  $\pi_w$  define the expanding pressures of oil and water respectively. For a flat film these are not equal. Because of the difference in the surface tensions of water and oil, the film will bend until the expanding pressures of water and oil are equal. If  $\pi_0 > \pi_w$ , the area at the oil side will expand until  $\pi_0 = \pi_w$ . Under these circumstances a w/o microemulsion is formed. This situation usually occurs if the surfactant used in the microemulsion is more soluble in oil than in water, i.e. if it has bulky hydrophobic groups. If  $\pi_0 < \pi_w$ , the area at the waterside

expands until  $\pi_0 = \pi_w$ . In this case an o/w microemulsion is formed. This often occurs when water-soluble surfactants are used. The type (w/o or o/w) of microemulsion formed therefore depends on the bending or curvature of the interface. A rough generalisation, known as Traube's rule, is that for a particular homologous series of surfactants, the concentration required for an equal lowering of surface tension in a dilute solution decreases by a factor of about 3 for each additional CH<sub>2</sub> group. If the interfacial tension between two liquids is reduced to a sufficiently low value on addition of a surfactant, emulsification will take place readily. This is because only a relatively small increase in the surface free energy of the system is involved. A thermodynamic definition of a microemulsion can be obtained from a consideration of the energy and entropy involved in the formation of microemulsions. Consider the diagrams in Figure 2.6 below.



**Figure 2.6: Diagrammatic illustration of the formation of microemulsions**

On the diagram  $A_1$  represents the surface area of the bulk water phase and  $A_2$  is the total surface area for all the microemulsion droplets.  $\gamma_{12}$  is the w/o interfacial tension. The increase in surface area when going from state A to B is  $\Delta A = (A_2 - A_1)$  and the surface energy increase is equal to  $\Delta A \gamma_{12}$ . The increase in entropy when going from state A to B is  $T \Delta S^{conf}$ . According to the second law of thermodynamics, the free energy of the formation of microemulsions,  $\Delta G_m$ , is given by the following expression:

$$\Delta G_m = \Delta A \gamma_{12} - T \Delta S^{conf} .$$

With traditional emulsions:

$$\gamma_{12}\Delta A \gg T\Delta S^{conf} \text{ and } \Delta G_m > 0$$

the system is non-spontaneous; it requires energy for the formation of the emulsion drops and it is thermodynamic unstable. With microemulsions  $\Delta A\gamma_{12} \leq T\Delta S^{conf}$ , this is due to the ultra-low interfacial tension accompanying the formation of microemulsions and  $\Delta G_m \leq 0$ . The system is produced spontaneously and it is thermodynamically stable. With emulsions, an increase in the mechanical energy and an increase in the surfactant concentration usually result in the formation of smaller droplets that become kinetically more stable.

Microemulsions are based on a specific combination of surfactants and a specific interaction with the oil and water phases, and the systems are produced spontaneously at optimum composition. The driving force for microemulsion formation is the low interfacial energy, which is overcompensated by the negative contribution entropy of dispersion term. The low interfacial tension is produced in most cases by a combination of two molecules, referred to as surfactants and cosurfactants (medium-chain alcohol).

### **2.8.5 Factors affecting the formation of microemulsions**

#### **i. Effect of surfactant nature**

The formation of a microemulsion is strongly dependent on the chemical nature of both the surfactants and the oil (Li and Wang, 1999; Bastogne and David, 1998; Eastoe *et al.*, 1997). Li and Wang studied the solubilization of w/o microemulsions formed with mixed surfactants containing one anionic and one cationic surfactant and an alcohol, as a function of the alkyl chain length of oil and mixed surfactants (sodium dodecyl sulphate [SDS] and cetyltrimethylammonium bromide [CTAB]). They found that the solubilization of water in microemulsion systems increases significantly with the mixed surfactants. This is due to the synergistic effect resulting from the strong Coulombic interactions between cationic and anionic surfactants (Li and Wang, 1999).

#### **ii. Effect of HLB**

Two different approaches to surfactant selection can be considered in order to achieve a high level of water solubilization in w/o microemulsions. The first approach is to maximise the amount of surfactant in the HLB 9-13 region, where it is intermediate between high oil solubility and high water solubility. The second approach is to use mixtures of highly oil-soluble surfactants and highly water-soluble surfactants. The latter mixture has been found to achieve the maximum water solubilization, evidently overcoming the expected partitioning of the two surfactant components into the oil and water phases and enhancing their partitioning to the interface [Huibers and Shah, 1997; Leon, 1977].

### **iii. Effect of oil type**

The stability of w/o microemulsions seems to be dependent on the molecular weight of the oil (De Castro Dantas *et al.*, 2001; Warisnoicharoen *et al.*, 2000). By increasing the length of the oil chain, the solubilization in water decreases, and the chain length is compatible when the system contains a medium-chain alcohol (Li and Wang, 1999). It was also observed that the microemulsion phase diagram for triglyceride oils of high molecular weight gives smaller homogeneous regions of w/o microemulsions than of esters and hydrocarbons of low molecular weight.

Stable self-emulsifying w/o microemulsions of extremely small particle size (5-30 nm), consisting of oil and a blend of a low and high hydrophilic-lipophilic balance (HLB) surfactants were studied by Panayiotis and Scalart (1997). The oil phase contained long or medium-chain triglycerides and mono-/diglycerides or sorbitan esters (low HLB surfactants). Polysorbate 80 (Tween 80) was used as a high-HLB surfactant (Constantinides and Scalart, 1997)

### **iv. Effect of cosurfactant**

Most microemulsions appear to form readily in the presence of a cosurfactant (Friberg *et al.*, 1999). It is asserted that this material partitions itself between the oil phase and the interface (Knickerbocker *et al.*, 1979; Watt *et al.*, 1998; Leon, 1977; Gu Guoxng, 1998; Alany *et al.*, 2000; Jihu Yao and Romsted, 1997; Sabatini *et al.*, 2003). In so doing it substantially changes the composition of the oil so that its interfacial tension with water is reduced. Binding of alcohol molecules to surfactant aggregates decreases their interfacial free energy and enhances the solubility of water and oil in w/o and o/w microemulsions respectively (Jihu

Yao and Romsted, 1997). The distribution of alcohols between the aggregates, oil and water of microemulsions depends on the chain length of the alcohols and hydrocarbons (Jihu Yao and Romsted, 1997; Puig *et al.*, 2003; Herrera *et al.*, 2003).

Most commonly used cosurfactants are medium-chain alcohols (Binks *et al.*, 2003). Materials such as short-chain fatty acids and alcohols are soluble in both water and oil (e.g. paraffin hydrocarbons) solvents. A molecule with two distinct parts, which are relatively polar and nonpolar, respectively, is called an *amphiphile*. This name is often reserved for molecules with easily perceptible surface activity at the air-water interface, i.e. molecules that preferentially absorb from aqueous solution into the air-water interface and lower its tension. Although the lower-molecular-weight alcohols such as methanol, through hexanol, are not generally classified as surfactants, they are in fact surface active at the air-water interface. They are certainly amphiphiles, possessing both hydrophilic and lipophilic moieties (Knickerbocker *et al.*, 1979).

The hydrocarbon part of the molecule is responsible for its solubility in oil, while the polar – COOH or -OH group has sufficient affinity to water to drag a short-length non-polar hydrocarbon chain into aqueous solution with it. If these molecules become located at the oil-water interface, they are able to locate their hydrophilic head groups in the aqueous phase and allow the lipophile hydrocarbon chains to escape into the oil phase. In general, the longer the hydrocarbon chain, the greater is the tendency for the alcohol molecules to adsorb the air-water surface and, hence, lower the surface tension. Most studies of alcohol-containing o/w and w/o microemulsions concluded with a fast exchange of the alcohol between the interfacial films, the continuous phase or the dispersed phase.

In the case of a w/o microemulsion made up of water/SDS/butanol/toluene, the addition of NaCl to the dispersed phase was found to slow down the alcohol exchange, perhaps because the interfacial film was then more compact (Friberg and Bothorel, 1987). In the case of microemulsions in which the alcohol/surfactant weight ratio was kept constant, the relaxation time for the cosurfactant exchange showed a continuous change upon increasing the oil content; including the range in which the o/w microemulsion turned into a w/o microemulsion. By contrast, for microemulsions in which the water/surfactant weight ratio

was kept constant, the relaxation went through a broad maximum at the water volume fraction corresponding to the w/o–o/w inversion.

The difference in behaviour may be related to the fact that in the latter system, the droplet size changes only slightly, with the water content in the w/o range, whereas large changes in the droplet size are expected to occur in the former system. These changes may modify the variation of the alcohol exchange relaxation time with composition (Friberg and Bothorel, 1987). In a study conducted by Nave *et al.* (2000) it was found, however, that some microemulsion systems could be formed without the presence of a cosurfactant. Nave *et al.* studied why Aerosol-OT is such an efficient surfactant for forming microemulsions. In pursuit of this, they investigated 11 Aerosol-OT-related surfactants. These surfactants were from two homologous series, with either linear or branched hydrocarbon tails.

With the linear dichain compounds, w/o microemulsion phases could be formed in the presence of a short-chain alcohol. On the other hand, all the branched surfactants formed microemulsions even in the absence of a cosurfactant. They therefore concluded that with regard to microemulsion formation, Aerosol-OT is not a special case, but it possesses a chain structure that gives optimum aqueous-phase solubility around room temperature (Nave *et al.*, 2000).

#### **v. Effect of alcohol chain length**

The solubilization of w/o microemulsions has been studied to elucidate how various components of microemulsions influence the spontaneous curvature and elasticity of interfacial films. It is inferred that the addition of a small amount of alcohol at optimal salinity, together with the condition of chain length compatibility, can result in the largest possible brine solubilization in a given w/o microemulsion (Leung and Shah, 1987). Alcohol is essential in promoting interfacial fluidity for the formation of microemulsions. It was found that decreasing the alcohol chain length in a microemulsion system leads to a decrease in the radius of the droplets and an increase in the interfacial fluidity.

In contrast, increasing the alcohol chain length may lead to an increase in the droplet size and a rigid interface. It appears that a small change in the alcohol chain length can strongly

influence the interfacial elasticity and hence the phase behaviour of microemulsions. For alcohols that promote interfacial fluidity, increasing the alcohol partitioning at the interface can increase the fluidity of the interface.

The addition of an alcohol (cosurfactant) can increase the total interfacial area at low alcohol concentration, thus increasing solubilization (Bastogne and David, 1998). However, at higher alcohol concentrations, phase separation occurs at a small droplet size due to the increase in attractive interdroplet interaction. Leung and Shah (1987) studied the effect of pentanol concentration on solubilization in a microemulsion containing hexadecane, octane and benzene. The solubilization showed a maximum as a function of pentanol. The maximum was most pronounced for the dodecane system due to the chain-length compatibility effect. Increasing the alcohol concentration can increase the alcohol partitioning at the interface, and consequently increase the total interfacial area available for solubilization. However, at sufficiently high concentrations, the fluidity of the interface increases, and hence solubilization decreases.

Kumar and Singh (1990) studied the influence of alkyl chain branching of the cosurfactant on the solubilizing capacity of a w/o microemulsion formed from fatty acid soaps. They found that branching in the cosurfactant chain decreased the water solubilization capacity. The solubilization behaviour was interpreted in terms of the partitioning of the alcohol among the oil, water and interface, depending on the chain length of the oil and surfactant. The molar ratio of the alcohol to surfactant at the droplet interface was found to increase with the length of the oil chain.

W/o microemulsions were produced by mixing different combinations of the cationic surfactants cetyltrimethylammonium bromide and cetylpyridinium chloride, *n*-alkanes (C<sub>5</sub> – C<sub>7</sub>) and benzene as oils, and *n*-alkylamines (C<sub>6</sub> – C<sub>8</sub>) and cyclohexylamine as cosurfactants with water (Singh *et al.*, 1993). The influence of the chain length of the alkanes and amines on the water solubilization behaviour of these systems was investigated. The solubilization of water in a particular microemulsion system is governed by the partitioning of amines among the oil, water and interfacial phases. The molar ratio of amine to surfactant and the droplet interface increased with the length of the oil chain.

**vi. Effect of salt concentration**

The effect of salt concentration on the solubilization of w/o microemulsions has been extensively studied by many researchers (Leung and Shah, 1987; Watt *et al.*, 1998; Arra *et al.*, 1999). In general, increasing the concentration of salt causes a reduction in the total aqueous phase solubilized. Leung and Shah concluded that decreasing brine solubilization with increasing salinity is due to an increase in the interfacial rigidity with increasing salinity. A decreasing alcohol partitioning at the interface with increasing salinity may also contribute to the decrease in brine solubilization.

With increased salt concentration, the formation of w/o microemulsions is expected to be favoured. This is because the electrostatic interactions of the surfactant head groups are suppressed, causing the packing ratio to increase and inducing the formation of a w/o microemulsion (Watt *et al.*, 1998). However, excessive salt concentrations tend to drive the alcohol into the oil phase. Previous studies have suggested that this would limit the salt concentrations at which microemulsions can form.

The addition of salt to microemulsions is known to reduce the attractive interaction of the fluid interfaces and hence increase the solubilization (Leung and Shah, 1987). There is an optimal salinity for a given w/o microemulsion at which maximum brine solubilization occurs. For salinity lower than the optimal salinity, these effects, together with salting-out effects, tend to increase the solubilization. However, for salinity higher than optimal salinity, they increase the interfacial rigidity and curvature, thus decreasing the solubilization.

At low salinities the surfactant resides primarily at the water-rich phase of a two-phase mixture; at higher salinities the surfactant resides primarily in the hydrocarbon-rich phase of a two phase-mixture [Knickerbocker *et al.*, 1979]. It was reported that for alkyl aryl sulphonates, microemulsion phase behaviour correlates with ion size and charge, rather than with ionic strength alone. The limiting amounts of solubilized aqueous NaCl, NaNO<sub>3</sub>, MgCl<sub>2</sub> and AlCl<sub>3</sub> in Aerosol-OT have been measured as a function of the ionic strength of the electrolytes (Hamada *et al.*, 2001).

**vii. Effect of ionic strength**

The solubilization of water in a microemulsion is strongly dependent on the ionic strength (Hamada *et al.*, 2001). Hamid and Vera (1996) reported on the water uptake of w/o microemulsions in an Aerosol-OT system. They found that due to ion exchange between the cations in the aqueous phase and the presence of Na as a surfactant counter-ion, the water uptake was strongly affected by the nature and concentration of the cations and was insensitive to the nature of the anions.

Hamid and Vera reported that water uptake decreases significantly as the salt concentration increases. This is due to the ionic strength of the aqueous phase, which produces a charge density inside the reverse micelles. The repulsive forces between surfactant-charged heads are reduced: they come closer and the size of the reverse micelles [(w/o) microemulsion] decreases, thus reducing the water uptake. Furthermore, different cations (even cations with the same charge and approximately the same hydrated size, such as  $K^+$  and  $Cs^+$ ) produce significant differences in the water uptake. These salts alter the water uptake because they have cations different from those of  $Na^+$  (Hamid and Vera, 1996).

Hamada *et al.* (2001) measured the limiting amounts of solubilized aqueous NaCl,  $NaNO_3$ ,  $MgCl_2$  and  $AlCl_3$  in Aerosol-OT/isooctane, as a function of the ionic strength of the electrolytes. They found that in those systems, the limiting amounts increased up to the optimal ionic strength, and afterwards, as ionic strength increased, they decreased and were followed by a constant. They interpreted the increased and decreased curves of water solubilization, called *salting-in* and *salting-out curves* respectively; as the counteracting effects of attractive intermicellar interaction and interfacial bending stress (Hamada *et al.*, 2001).

In a study of surfactant selection for microemulsion flooding (Puerto, 1992), ionic strength effects were also investigated. They found that salt concentration in microemulsion systems has strong influence in oil recovery since the water in oil reservoir is brine (Friberg and Bothorel, 1987). Plucinski and Nitsch (1994) studied the specific ion effect of the ion exchange in w/o microemulsion systems in the equilibrium state, as well as in kinetic experiments using a two-phase cell. The equilibrium results of an ion exchange revealed the importance of the specific ion adsorption at the negative Aerosol-OT layer. It was found that larger cations were much better adsorbed at the interface than smaller ones, independent of

their valency. The relevant interpretation states that reverse micelles present in the organic phase, colliding with the liquid/liquid interface to form channels between the aqueous pool of the micelles and the bulk aqueous phase. Then, after successful fusion, the micelles release themselves from the interface, completing the process of solubilization (Plucinski and Nitsch, 1994).

### **2.8.6 Conductivity of microemulsions**

Microemulsions have similar electric conductivity to that of conventional emulsions. Microemulsions with water as the dispersed medium show better conductivity. Those with an oily disperse medium exhibit worse conductivity. Xun Fu (1995) studied the conductivities of w/o microemulsions of the sodium salt of the mono (2-ethyl hexyl) phosphate/hexane/pentanol/water system. The conductivities were measured during the dilution process with varying amounts of water present. It was found that the viscosity does not change significantly if the microemulsion is continuously diluted, but does change significantly when different quantities of water are added at the beginning of microemulsion formation. The quantity of water added at the beginning affects the structure parameters of the microemulsions. Xun Fu (1995) reported conductivities of above 2000  $\mu\text{S}/\text{cm}$  in his study.

Micelle formation affects the conductance of ionic surfactant solutions for the following reasons.

- Counter-ions become kinetically a part of the micelle, owing to its high surface charge, thus reducing the number of counter-ions available for carrying the current and also lowering the net charge of the micelles.
- The retarding influence of the ionic atmospheres of unattached counter-ions on the migration of the surfactant ions is greatly increased on aggregation. (Mehta and Bala, 2000).

### 2.8.7 Microemulsion phase inversion

In practice, oils that are capable of being microemulsified invert by the slow addition of water from a fluid w/o dispersion through a viscoelastic gel stage to a fluid o/w microemulsion. It is in this area of inversion that the Schulman's microemulsions display a peculiar phenomenon. Beginning with a fluid w/o microemulsion, as water is added, they pass through a viscoelastic gel state. As more water is added, they invert to an o/w microemulsion, which is fluid again. According to Leon (1977), this process is reversible. This pattern is so well defined as to be a hallmark of the o/w microemulsion. The viscoelastic gel stage is where the surfactant monolayer separates oil and water domains in a microemulsion system (co-continuous system). Their optical properties, in combination with their rheological behaviour, make positive identification possible without instrumentation (Lim *et al.*, 1998).

Microemulsions may be changed from w/o to o/w and vice versa by varying some of the emulsification conditions (Bastogne and David, 2000). Several experimental studies have clearly shown that the so-called *microstructure* may be formed in the process of phase inversion. The bicontinuous structure is such a microstructure in which water and oil are locally continuous (Chunsheng *et al.*, 2000; Gutfelt *et al.*, 1997; Wolfgang, 1995; Burauer *et al.*, 2003).

Cosurfactant partitioning seems to be very important, both for the nature of the phases formed and for the microemulsion structure. The latter could be rather well illustrated from self-diffusion studies. This type of study, which involves measurements for different lengths of an *n*-alcohol cosurfactant at a fixed molar ratio between the four components, was done for a number of systems. With butanol and pentanol as cosurfactants, a situation with the diffusion (*D*) of water and hydrocarbon only differing by a small factor was encountered.

For a long-chain alcohol, on the other hand, hydrocarbon diffusion is more rapid than water diffusion by a factor of more than 100. Consequently, a medium-chain alcohol has a strong tendency to favour a bicontinuous structure, while a long-chain alcohol confers on the system a w/o structure with discrete droplets. At low salinities  $D_{\text{water}} \gg D_{\text{hydrocarbon}}$ , an o/w structure applies. At high salinities, the opposite situation is encountered, i.e.  $D_{\text{hydrocarbon}} \ll D_{\text{water}}$ . At intermediate salinities, a bicontinuous structure results since  $D_{\text{hydrocarbon}} \sim D_{\text{water}}$ , both being high (Friberg and Bothorel, 1987; Billman and Kaler, 1991).

### 2.8.8 Application of microemulsions

In recent years, micellar solutions and microemulsions have been investigated as reaction media for various chemical reactions, including polymerisation (Karin *et al.*, 1998; De Buruaga *et al.*, 2000). Early work was carried out in the 1970s (Fanun, 2001). Among these investigations, a particularly challenging field was the use of microemulsions in biocatalysis. It has been shown that three aspects can describe the influence of structured fluids on the chemical reactions:

- ❑ Solubilization of a broad spectrum of substances in a homogeneous system to overcome reagent incompatibility problems.
- ❑ Enhancement of the specific rate of reaction due to the partitioning and concentration of the reactants and products.
- ❑ The structure of the fluid, which influences reaction region selectivity due to the orientation of the reactants at the interfacial region.

Microemulsions have been employed in various pharmaceutical techniques, including drug delivery (Kang *et al.*, 2004; Sintov and Shapiro, 2004; Gupta *et al.*, 2004; Valenta and Schultz, 2004; Cantarovich *et al.*, 2004; Ogino *et al.*, 2004). In a study conducted by Guo-Wei *et al.* (2001) it was established that many enzymes could be entrapped in w/o microemulsions or reverse micelles, retaining their catalytic activity.

Among the enzymes studied to date, lipases are the most attractive due to their numerous biotechnological applications in the preparation of fine chemicals, and in the food and pharmaceutical industries. One of the most intensively studied aspects has been the technique of solubilizing enzymes in w/o microemulsions. A major attraction of this procedure is that the lipase is dispersed at the molecular level, rather than as a solid aggregate, in a thermodynamically stable solution. This solution is capable of solubilizing polar, a polar and interfacially active substrates. The main advantages of this system are the possibility of providing the enzyme with an adequate environment, thereby protecting it against denaturation by organic solvents.

Microemulsions have found application in metal extractions and the oil recovery process (Castro Dantas *et al.*, 2003). They have also been studied extensively in the synthesis of nanometre-size particles (Lee *et al.*, 1992; Rees *et al.*, 1999; Lim *et al.*, 1998; Qi *et al.*, 1997;

Zhang and Gao, 2004; Cushing *et al.*, 2004; Hernandez, Solla-Gullon and Herrero, 2004; Huang *et al.*, 2004; He *et al.*, 2004; Caponetti *et al.*, 2003; Lee *et al.* 1992) prepared nanometre particles of Fe<sub>3</sub>O<sub>4</sub> in Aerosol-OT/ water/iso-octane w/o microemulsions. Spherical copper nanoparticles were synthesised in an SDS/isopentanol/cyclohexane/water microemulsion with sodium borohydride as a reducing agent (Qui *et al.*, 1999). Various microemulsion formulations were evaluated as reaction media for the synthesis of the surface-active compound decyl sulphonate from decyl bromide and sodium sulphite (Gutfelt *et al.*, 1997). The reaction rate was reported to be fast, both in w/o microemulsions and in bicontinuous microemulsions based on non-ionic surfactants.

### 3. EXPERIMENTAL

The experiments were designed as follows:

- Make microemulsions of different salts at different concentrations using two surfactant systems.
- The surfactant systems used were: nonyl phenol ethoxylated phosphate ester (ATPOL 3205) and didecylammonium chloride (DDAC).

#### 3.1 ATPOL 3205 system

The ATPOL system contains Shellsol oil, alcohol and diethanolamine to neutralise the surfactant. This four-component system is referred to as the oil phase. The alcohol acts as a cosurfactant. The alcohol chain lengths (butanol, hexanol and octanol) were varied to study the effect. The following salt combinations were investigated at different concentrations:

1. Diethanolamine nitrite salt
2. Diethanolamine sulphate salt (0,125 M, 0,25 M, 0,5 M, 1.0 M, 2.0 M, 3.0 M and 4.0 M)
3. Diethanolamine phosphate (0,125 M, 0,25 M, 0,5 M, 1.0 M, 2.0 M, 3.0 M and 4.0 M)

The salts were formed by reacting diethanolamine with their respective counter-ion salts at stoichiometric mole ratios. The reason for using diethanolamine as a carrier for the ions was to decrease the polarity of the water phase in order to increase water phase solubilization in the oil phase.

The oil phase was titrated with a series of known amounts of salt solution in a poly-top and observed after at least 24 hours for phase separation. This was done for each salt at different concentrations. The butanol in the oil phase was replaced by hexanol and octanol, and the experiment was repeated for each alcohol whilst maintaining the same number of moles of alcohol in the micromulsion. The titration method of making microemulsion is a conventional used by many researchers to make microemulsions.

#### 3.2 DDAC (Quat) system

In this system the twin-chain Quat surfactant didecyltrimethyl ammonium chloride (DDAC) was used. The Quat system oil phase consists of surfactants, Shellsol oil and alcohol (butanol

or hexanol). The following salts were prepared and used as the aqueous phase.

1. Ammonium acetate salt (0.25 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M and 4.0 M)
2. Sodium acetate (0.25 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M and 4.0 M)
3. Zinc acetate (0.5 M, 1.0 M, 2.0 M, 3.0 M, 4.0 M)
4. Magnesium acetate (0.5 M, 1.0 M, 2.0 M)

The oil phase was titrated with a series of known amounts of salt solution and observed after at least one week, for phase separation. This was done for each salt at all concentrations. The butanol in the oil phase was replaced by hexanol and the experiment was repeated for each alcohol for most salts.

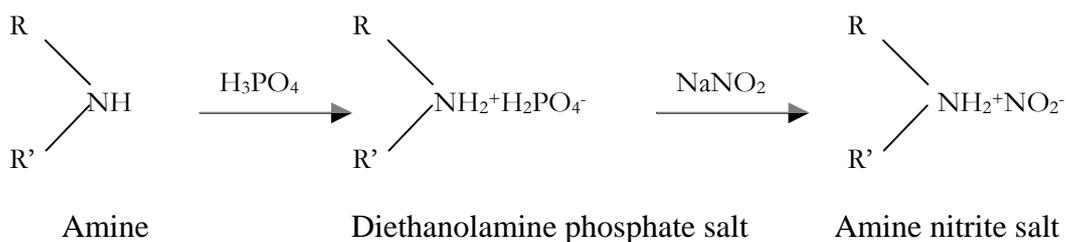
### **3.3 Preparation of the Amine Nitrite Salts**

#### **3.3.1 Apparatus**

- ❑ An accurate scale and some laboratory glassware
- ❑ A separating funnel to separate the amine nitrite salts from the water
- ❑ A desiccator for drying the amine nitrite salts
- ❑ A glass membrane for separating the crystals from the amine nitrite salt
- ❑ A vacuum suction set-up for separation with a glass membrane
- ❑ A hotplate with magnetic stirrer.

#### **3.3.2 Planning**

Mainly secondary amines were used to form the nitrite salts, according to the two-step reaction shown in Scheme 1.



**Scheme 1: Reaction of secondary amine with nitrite ion to form amine nitrite salt**

The neutralisation reaction with phosphoric acid is necessary because a direct reaction with nitrite will form nitrosamines. These are carcinogenic and are not the desired product. The amine nitrite salt is mixed with some Shellsol oil to determine its ability to form a homogeneous mixture with this solvent. A few drops of butanol can be added to aid the mixing process. The fairly water-soluble amine nitrite salts will not separate from water, but form a mixture of water and salt. This needs to be desiccated.

**3.3.3 Standard procedure for making amine nitrite salt**

- ❑ Place about 2 g of the amine in a poly-top in a cold water-bath ( $\pm 10^\circ\text{C}$ ).
- ❑ Add about 1.5 g of distilled water.
- ❑ Add an equivalent amount of  $\text{H}_3\text{PO}_4$  (85%) while stirring and monitoring the pH until a pH of about 6.5 to 7 is reached. Universal indicator paper is sufficient. (Equivalence is calculated from molar masses.)
- ❑ Add an equivalent amount of  $\text{NaNO}_2$  and stir well.
- ❑ Seal the poly-top and leave it overnight. If the amine nitrite salt does not separate from the water, add excess  $\text{NaNO}_2$  to make the water ionic and force the non-polar groups to phase separate from the water.

**3.3.4 Procedure for drying amine nitrite salts that are water soluble**

- ❑ Separate the amine nitrite salt from the aqueous layer with a separating funnel. Dry this mixture over  $\text{P}_2\text{O}_5$  in a desiccator for a few days.
- ❑ If crystallisation occurs, the amine nitrite needs to be filtered through a glass membrane with vacuum suction.

### **3.3.5 Procedure for testing miscibility with the oil phase**

- ❑ Add a few drops of the amine nitrite salt to some Shellsol oil (or xylene) and mix thoroughly.
- ❑ Allow settling time to let the mixture reach its most stable form.
- ❑ A few drops of butanol can be added as cosurfactant if phase separation occurs.

### **3.3.6 Checking to ensure that amine nitrite salt has been formed**

A yield calculation is done with DIBA (di-isobutyl amine), which is not soluble in water. This amine is chosen because the amine nitrite salt layer formed contains minimal amounts of water.

## **3.4 Preparation of Microemulsions Containing Amine Nitrite**

Samples are mixed in poly-tops, each with its own glass rod to avoid contamination and wastage. Enough of each sample needs to be made in order for the spindle of the viscosity meter to be submerged in the sample to the right level. These samples are placed in a temperature-controlled water-bath to ensure constant temperature for viscosity measurements.

Microemulsions form spontaneously. However, phase separation often takes somewhat longer due to the high viscosity of ATPOL's oil phase. The samples are therefore left for at least 24 hours (wherever possible) in order to allow phase separation to occur. ATPOL surfactants are acidic and need to be neutralised. Diethanolamine is therefore incorporated in the oil phase to neutralise the surfactant. The microemulsions are shear thinning and the spindle rotating in the sample creates shear force. This leads to the viscosity decreasing with time while the spindle is rotating. All readings need to be taken after the same duration of rotation time to avoid experimental error, e.g. after 1 minute.

### **3.4.1 Apparatus**

- ❑ A conductivity meter
- ❑ A viscosity meter and stop watch
- ❑ A water-bath
- ❑ Poly-tops and glass rods.

### **3.4.2 Titration of the surfactant**

A few grams of the oil phase are mixed with an equal amount of water and some phenolphthalein as indicator.

The mixture is titrated with a 25% solution of sodium hydroxide (NaOH) until the equivalence point is reached and the solution turns from clear to a bright pink.

### **3.4.3 Mixing of the samples**

Mixing is done according to mass fractions unless otherwise stated. The oil and water phases are prepared separately. A total of about 16 g are made per sample. The oil phase is first weighed in a poly-top and then titrated with the aqueous phase. The water phase is then added successively. The sample is left for at least 24 hours before measurements are taken.

### **3.4.4 Measurements**

All measurements are done at 30 °C. The mixtures are placed in a water-bath for at least 12 hours before the measurements are taken. The laboratory is at about 25 °C, so cooling is minimal.

#### **i Viscosity**

Viscosity is measured using the same spindle for all samples. The spindle is placed in the sample and the motor is switched on. After 30 s the reading is taken.

#### **ii Conductivity**

The conductivity reading is taken once the mixture has stabilised. Care is taken to ensure there are no air bubbles around the electrode and in cleaning the electrode.

## **3.5 Microemulsion Phase Ratios and Concentrations of Salts (ATPOL System)**

### **3.5.1 Oil phase used**

- ATPOL 3202 Surfactant (12.7 parts)
- Shellsol oil (2.7 parts)
- Alcohol (butanol 2.7 parts, hexanol 3.48 parts, octanol 4.4 parts)
- Diethanolamine (3.0 parts).

### 3.5.2 Aqueous phase

1.  $\text{H}_2\text{SO}_4^{2-}$  + Diethanolamine  $\rightarrow$  Diethanolamine sulphate
2.  $\text{H}_3\text{PO}_4^{3-}$  + Diethanolamine  $\rightarrow$  Diethanolamine phosphate

(All at 0.125 M, 0.25 M, 0.5 M, 2 M, 3 M and 4 M)

Determine the point at which microemulsion phase separation occurs for each concentration and change the alcohol chain length for selected concentrations by titrating the oil phase with the aqueous phase.

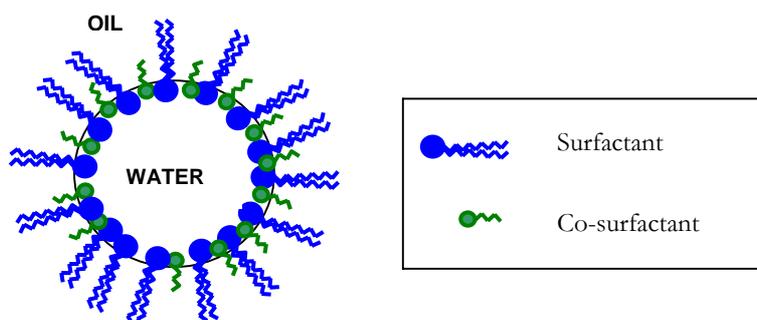
### 3.5.3 Preparation of the aqueous phase

Prepare ~30% amine nitrite by reacting sodium nitrite with diethanolamine and use as the aqueous phase. Titrate the ATPOL oil phase with this solution to make up 23% sodium nitrite in the microemulsion.

## 4. RESULTS AND DISCUSSION

### 4.1 Formation of w/o Microemulsion Containing Amine Nitrite Stabilised by ATPOL Surfactant

A microemulsion is a special form of dispersion. It is a mixture of polar and non-polar media, which is stabilised by a surfactant and a cosurfactant, which together form the interface. Figure 4.1 shows a schematic representation of a w/o dispersion. The surfactant used in this application is an amphiphile with two hydrophobic tails. By neutralisation it becomes ionic and has a charged hydrophilic head. Repulsion between the heads is minimised by the cosurfactant, for instance an alcohol. The surfactant aggregates with the aqueous phase, forming structures like reversed micelles. The size of the microemulsion aggregates is between that of a micelle and a normal emulsion, namely between 5 and 50 nm.

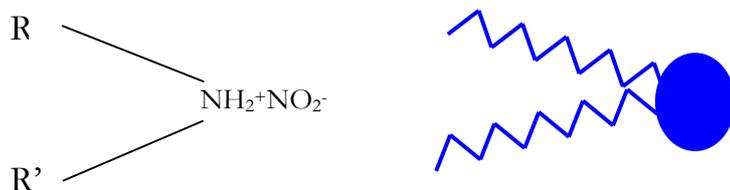


**Figure 4.1: Schematic representation of a water-in-oil microemulsion. Water droplets are dispersed in the main medium of oil**

A ternary system of the oil phase, the water phase and the surfactant-cosurfactant mixture only forms single-phase microemulsions for certain compositions. This is dependent on many factors, including:

- ❑ The oil chain length
- ❑ The surfactant type and its chain length
- ❑ The hydrophilic head group
- ❑ The structure of the cosurfactant
- ❑ The salt concentration in the aqueous phase
- ❑ The ratio of surfactant to cosurfactant
- ❑ The temperature.

From Figure 4.1 (Microemulsions) it can be seen that the surfactant has a hydrophilic head and two hydrophobic tails. This implies that the nitrite salt of the secondary or possibly also tertiary amines is suitable. The nitrite group is hydrophilic and the two organic groups form the hydrophobic tails. This is shown in Figure 4.2 below. The advantage of these salts is their nitrite content.



**Figure 4.2: Structure of an amine nitrite salt and the surfactant**

#### 4.1.1 Formation of amine nitrite

The amine nitrite was formed according to the two-step reaction shown in Scheme I. The neutralisation reaction with phosphoric acid is necessary because a direct reaction with nitrite will form nitrosamines.

**Table 4.1: Results of the yield calculation for di-isobutyl amine nitrite salt**

| Reagent/<br>Product            | Mass used/<br>formed<br>[g] | Molar mass<br>[g/mol] | Mole<br>used/formed<br>[mol] | Yield<br>[%] |
|--------------------------------|-----------------------------|-----------------------|------------------------------|--------------|
| DIBA                           | 2.5                         | 129.3                 | 0.019                        |              |
| H <sub>3</sub> PO <sub>4</sub> | 2.0                         | 98.0                  | 0.020                        |              |
| NaNO <sub>2</sub>              | 1.4                         | 69.1                  | 0.020                        |              |
| DIBAN                          | 2.8                         | 176.3                 | 0.016                        | 81%          |

A check to ensure that the amine nitrite had formed was done with di-isobutyl amine. The results are displayed in Table 4.1 below. They prove that a reaction does take place, because the mass of the product is greater than that of the reagent. This implies that the molar mass of the reagent has increased. In all experiments similar changes are observed, namely a gel or precipitate forms after the acid has been added, and upon addition of the NaNO<sub>2</sub> the mixture becomes more liquid with a precipitate or immediate phase separation. All amine nitrite salts are yellow to orange in colour.

The results of the various amines tested are shown in Table 4.2 below. The nitrite content of the microemulsions in this application is given in terms of  $\text{NaNO}_2$  content, even though only the nitrite ion is of importance. It is therefore useful to determine the mass percentage of one amine nitrite salt molecule that is equivalent to one molecule of  $\text{NaNO}_2$ . This is calculated according to the following equation:

$$\% \text{NaNO}_2 \text{ equivalence} = \frac{FW_{\text{NaNO}_2}}{FW_{\text{amine nitrite salt}}} \times 100$$

For a compound to be miscible with water (a strong dipole), the non-polar groups need to have some affinity with water. Since the butyl chains of DIBA and DBA are not miscible with water, any compound with longer chains will not be miscible either. Only the amine nitrite salts of DBA, DIBA and DHA form homogeneous mixtures with Shellsol, whereas only DEtOHA and DEEA form salts that are sufficiently soluble in water. It can be seen quite clearly that the difficulty lies in obtaining an amine nitrite salt that is miscible with both water and Shellsol. Thus the mixing of a water-soluble amine nitrite salt with one that forms a homogeneous solution with Shellsol was also tested.

The water-soluble component should introduce the salt in the aqueous phase and the other component acts as surfactant to form a uniform mixture between water and oil. Butanol is added as cosurfactant to reduce the repulsion of the charged heads of the surfactant. The mixtures tried are shown in Table 4.3 below. A further test was done to determine the solubility of the amine nitrite salts in xylene instead of Shellsol. Xylene has only aromatic rings and should be more miscible with water-soluble matter than are aliphatic compounds. However, for the oil phase, this is not really a feasible solution because Shellsol, being a by-product of the industry, is significantly cost effective and has a higher flash point (above  $150^\circ\text{C}$ ).

The action of butanol as a cosurfactant is not strong enough to stabilise the interface. The best results are achieved with DBAN and DEEAN, in which stabilisation and phase separation takes the longest. Mixing of the above water-miscible and Shellsol-miscible amine nitrite salts does not lead to a stable microemulsion.

**Table 4.2: Amines used to make amine nitrite salts and the results of the suitability test**

| <b>Amine</b>                            | <b>Code</b> | <b>Molar mass</b> | <b>NaNO<sub>2</sub> equivalent (%)</b> | <b>Shellsol Miscibility</b> | <b>H<sub>2</sub>O Miscibility</b> |
|---|-------------|-------------------|--|-----------------------------|-----------------------------------|
| Dibutyl amine                           | DBA         | 129.25            | 39.15                                  | Yes                         | No                                |
| Diisobutyl amine                        | DIBA        | 129.25            | 39.15                                  | Yes                         | No                                |
| Diisobutyl amine +<br>Dibutyl amine 1:1 | DBA-DIBA    | 129.25            | 39.15                                  | Yes                         | No                                |
| Morpholine                              | MOR         | 87.12             | 51.44                                  | No                          | No                                |
| Diethylethanol amine                    | DEEA        | 117.19            | 42.02                                  | No*                         | Yes                               |
| Dicyclohexyl amine                      | DICHA       | 181.32            | 30.22                                  | No                          | No                                |
| Ethylidicyclo- hexyl amine              | EDCA        | 209.37            | 26.91                                  | No                          | No                                |
| 2 Ethanol-piperidine                    | EP          | 129.20            | 39.16                                  | No                          | No                                |
| Di-n-hexyl amine                        | DHA         | 185.00            | 29.74                                  | Yes                         | No                                |
| Tri-n-butyl amine                       | TBA         | 185.00            | 29.74                                  | No                          | No                                |
| Diethanolamine                          | DEtOHA      | 105.15            | 45.35                                  | No*                         | Yes                               |

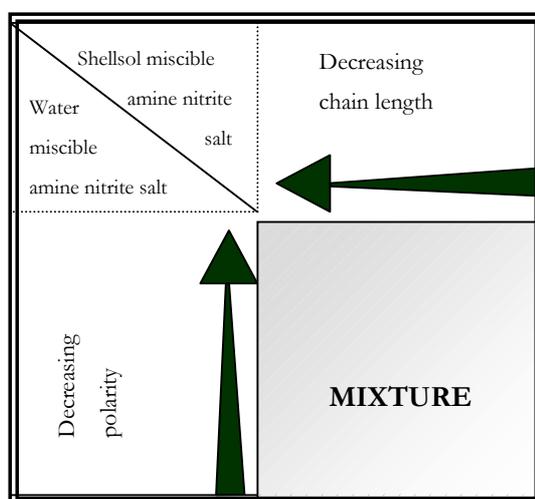
\* Addition of butanol does aid miscibility; Immiscible with xylene

**Table 4.3: Amine nitrite salt mixtures tested**

| <b>Nitrite</b> | <b>Mass ratio x:1</b> | <b>Shellsol-soluble component</b> | <b>Cosurfactant</b>       | <b>Results: Number of layers (phases)</b> |
|----------------|-----------------------|-----------------------------------|---------------------------|---|
| DEtOHAN        | 9                     | DBAN                              | ---                       | 2   |
|                |                       |                                   | Butanol                   | 3   |
| DEEAN          | 3                     | DBAN                              | ---                       | 2   |
|                |                       |                                   | Butanol                   | 3   |
| DEtOHAN        | 7.5                   | DHAN                              | ---                       | 2   |
| DEtOHAN        | 6.75                  | DHAN                              | ---                       | 2   |
|                |                       |                                   | Butanol                   | 2   |
| DEtOHAN        | 4                     | DHAN                              | ---                       | 2   |
|                |                       |                                   | Butanol, octanol, decanol | 3   |
| DEtOHAN        | 3                     | DHAN                              | Butanol                   | 3   |
| DEtOHAN        | 1.5                   | DHAN                              | Butanol                   | 3   |
| DEEAN          | 9                     | DHAN                              | ---                       | 2   |
|                |                       |                                   | Butanol                   | 3   |

Neither an amine nitrite salt, nor any mixture of such salts made, is miscible with both Shellsol and water. The best miscibility is achieved with DEEAN and DBAN. DEEAN is the less polar of the two water miscible salts and DBAN has shorter chains and is thus less non-polar than DHAN. This implies that amine nitrite salts with less extreme properties will mix the most easily.

In the matrix shown in Figure 4.3 below, the darker the shading of the area, the better the chances of finding a mixture that will work. Amines should be chosen keeping this in mind. A recommendation for the non-polar constituent is dipropyl or di-isopropyl amine, and for the polar constituent dipropylethanol amine.



**Figure 4.3: Mixing matrix for amine nitrite salts that can be used to make surfactants**

Although the amine nitrite salts cannot replace the surfactants, their nitrite content makes them attractive for use in the water phase as a source of nitrite. An investigation into the use of water-miscible amine nitrite salts in the water phase of microemulsions was completed.

#### **4.1.2 Preparation of w/o microemulsion with amine nitrite**

Table 4.4 below shows the oil phase and the aqueous phase for making the microemulsion with the ATPOL system. The oil phase chosen for most experiments was oil phase I, which contains the ATPOL E 3202 as surfactant. A series of samples were made with water phases of different  $\text{NaNO}_2$  concentrations to measure the viscosity and conductivity in order to determine the maximum  $\text{NaNO}_2$  content possible (Series A, B and C):

- From that starting point, oil phases II and III were trials of a 15% increase and decrease in the amount of cosurfactant respectively.
- The next series, F, consisting of different surfactants, was done to test the suitability of surfactants. The mixing for oil phases IV to IX was as follows:
  - Surfactant to butanol → 1: 1 (molar basis)
  - (Surfactant + butanol) to Shellsol → Same ratio as standard oil phase
- ATPHOS E 3205 was then used in Series G, but in exactly the same mixing ratio as in the standard oil phase to do a series of viscosity measurements (oil phase X).
- The next experiment (named H) was done using salts as the water phase. For this the standard oil phase (I) and also the ATPHOS oil phase (X) were used. An additional water phase was added successively until phase separation occurred.
- The last range of samples was made with oil phases I and X and water phases containing both amine nitrite salts and  $\text{NaNO}_2$  in water. Two series were done with water phases of different  $\text{NO}_2$  contents. The mixing ratios were as follows:
  - $\text{NaNO}_2$  to amine nitrite salt → 1: 1 (molar basis)
  - K → 1 mol  $\text{NaNO}_2$ : 1 mol amine nitrite salt: 2.5 mol water
  - L → 1 mol  $\text{NaNO}_2$ : 1 mol amine nitrite salt: 3.0 mol water

Again the water phase was added successively until phase separation occurred.

The results were used to calculate the amount of NaOH/diethanolamine required for neutralising the oil phase of each sample and this amount was then added to the water. The results are given in Table 4.5.

In calculating the  $\text{NaNO}_2$  content of the microemulsions, the mass of NaOH/diethanolamine added to the sample is not included. It is more or less the same for each sample and constitutes only about 3% of the total mass.

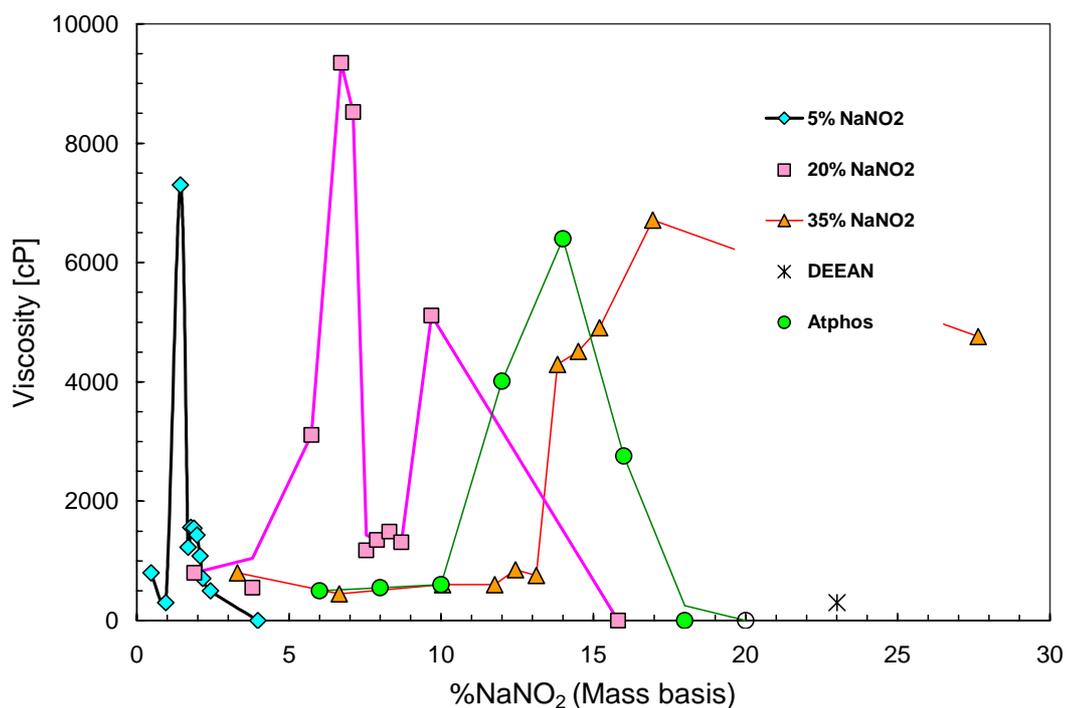
The results for the viscosity in the series A, B, C and G are graphically displayed in Figure 4.4. The solid markers indicate the single-phase and the hollow markers the two-phase samples.

**Table 4.4: The different oil phases used**

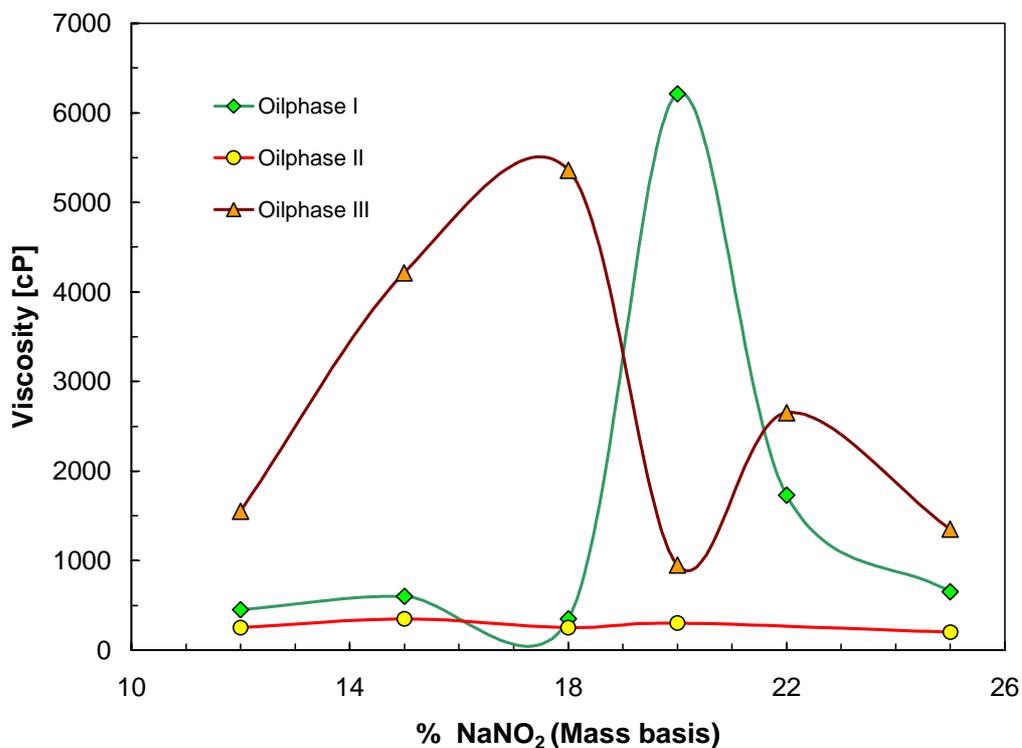
| No. | Surfactant  | Mass percentages |         |          | Series | Water phase                                       |
|-----|---|------------------|---------|----------|--------|---|
|     |   | Surfactant       | Butanol | Shellsol |        |   |
| I   | Atpol E 3202  | 66.7             | 19.4    | 13.9     | A      | 5% NaNO <sub>2</sub> in water                     |
|     |   |                  |         |          | B      | 20% NaNO <sub>2</sub> in water                    |
|     |   |                  |         |          | C      | 35% NaNO <sub>2</sub> in water                    |
|     |   |                  |         |          | D & E  | 40% NaNO <sub>2</sub> in water                    |
|     |   |                  |         |          | H      | DEtOHAN & DEEAN                                   |
|     |   |                  |         |          | K & L  | DEtOHAN and DEEAN with NaNO <sub>2</sub> in water |
| II  | Atpol E 3202  | 64.9             | 21.6    | 13.5     | D & E  | 40% NaNO <sub>2</sub> in water                    |
| III | Atpol E 3202  | 68.6             | 17.1    | 14.3     | D & E  | 40% NaNO <sub>2</sub> in water                    |
| IV  | Dowfax 3B2  | 81.1             | 5.0     | 13.9     | F      | 30% NaNO <sub>2</sub> in water                    |
| V   | Atpol E 1231  | 83.5             | 2.7     | 13.9     | F      | 30% NaNO <sub>2</sub> in water                    |
| VI  | Atpol E 3205  | 79.0             | 7.1     | 13.9     | F      | 30% NaNO <sub>2</sub> in water                    |
| VII | CTC 30<br>(Incroquat)                                     | 63.4             | 15.3    | 21.3     | F      | 30% NaNO <sub>2</sub> in water                    |
| IIX | DDDDMAB<br>Didodecyl-<br>dimethyl-<br>ammonium<br>bromide | 75.9             | 10.2    | 13.9     | F      | 30% NaNO <sub>2</sub> in water                    |
|     |   |                  |         |          |        |   |
| IX  | DSEHSS<br>sodium-2-<br>ethylhexyl-<br>sulphosuccina<br>te | 72.4             | 17.2    | 10.4     | F      | 30% NaNO <sub>2</sub> in water                    |
| X   | Atpos E<br>3205   | 66.7             | 19.4    | 13.9     | G      | 30% NaNO <sub>2</sub> in water                    |
|     |   |                  |         |          | H      | DEtOHAN & DEEAN                                   |
|     |   |                  |         |          | K & L  | DEtOHAN and DEEAN with NaNO <sub>2</sub> in water |

**Table 4.5: Amounts of sodium hydroxide/diethanolamine needed for the different surfactants**

| Oil phase | Surfactant    | Approximate pH | Mass of sodium hydroxide per gram of oil phase [g] |
|-----------|---------------|----------------|--|
| I         | Atpol E 3202  | 2.5            | 0.0615   |
| II        | Atpol E 3202  | 2.5            | 0.0524   |
| III       | Atpol E 3202  | 2.5            | 0.0664   |
| IV        | Dowfax 3B2    | 4              | 0.035  |
| V         | Atphos E 3205 | 2.5            | 0.0615   |
| VI        | CTC 30        | 4.5            | 0.03   |
| VII       | Atpol E 1231  | 5.5            | 0.018  |
| VIII      | DDDDMAB       | 4              | 0.032  |
| IX        | DSEHSS        | 6              | 0.012  |
| X         | Atphos E 3205 | 2.5            | 0.0615   |


**Figure 4.4: Viscosity of the microemulsion using oil phases I and X and different water phases.**

Generally, the viscosity increases slowly with an increase in the fraction of the water phase (and thus an increase in the  $\text{NaNO}_2$  content) in the sample. The viscosity reaches a point where it suddenly peaks and thereafter the microemulsions tend to become unstable and phase separation occurs. This is, however, not always detected in the experiments because the higher the viscosity, the more resistance there is to phase separation. After the peak in viscosity, the samples change from single-phase to two-phase and back again with increasing water phase content. The transition from a w/o to an o/w microemulsion occurs in this region. The samples in oil phase X show results very consistent with those of oil phase I. The graph has a similar shape and, when one looks at the concentration of the water phase, it lies in the expected region.



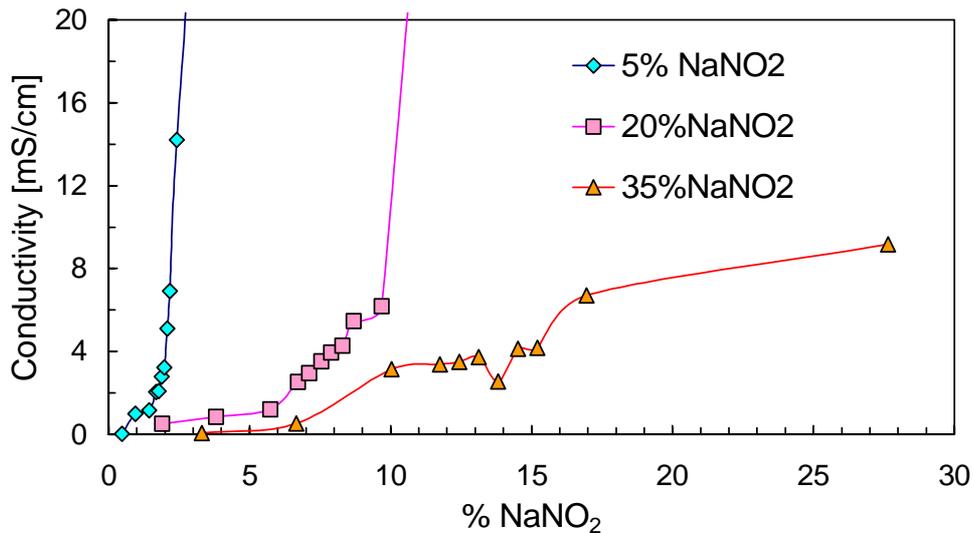
**Figure 4.5: Viscosity measurements of microemulsions with different oil phases containing a  $\text{NaNO}_2$  water phase.**

Oil phase I - standard oil phase with 40%  $\text{NaNO}_2$  in water; Oil phase II - about 15% more butanol with 40%  $\text{NaNO}_2$  in water; Oil phase III - about 15% less butanol with 40%  $\text{NaNO}_2$  in water

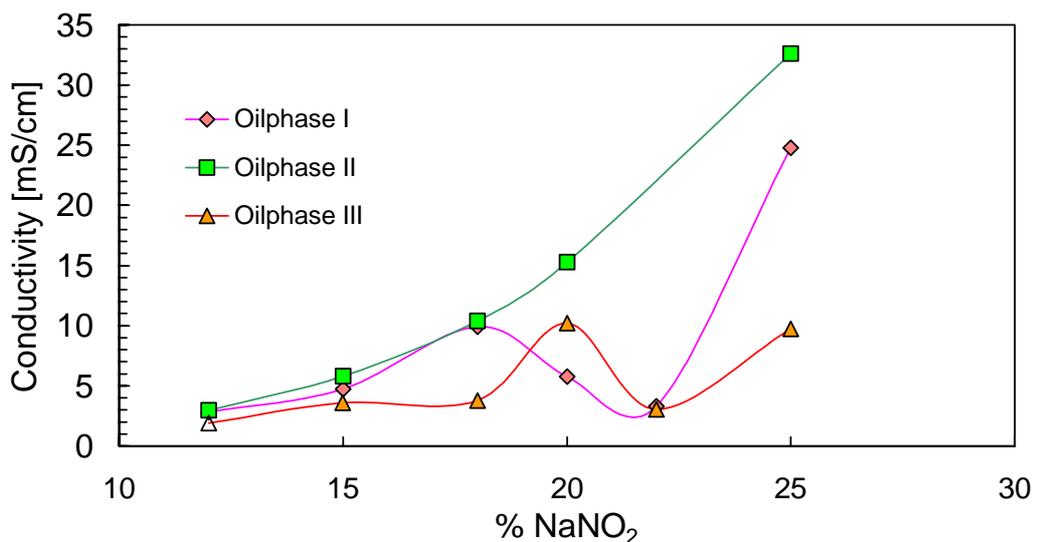
The results of Series D and E are shown in Figure 4.5 below. Again, solid markers represent the single-phase and hollow markers the two-phase samples. The conductivity was only

measured for the Series A, B, C, D and E. The results are displayed in Figures 4.6 and 4.7 below. Although the conductivity rises with increasing percentage of the water phase, no correlation with viscosity is detectable.

Of the experiments done in Series F, only the ATPHOS E 3205 oil phase formed a microemulsion. Series H and L each yielded one stable microemulsion. The results of Series H and L are displayed in Table 4.6.



**Figure 4.6: Conductivity of microemulsions using oil phase I and different water phases**



**Figure 4.7: Conductivity of microemulsions using different oil phases and a 40% NaNO<sub>2</sub> water phase.** Oil phase I - standard oil phase; Oil phase II - about 15% more butanol; Oil phase III - about 15% less butanol

**Table 4.6: Samples mixed with amine nitrite salts as water phase**

| Series H     | DEtOHAN                                |                        | DEEAN                                |   |
|--------------|--|------------------------|--------------------------------------|---|
|              | % NaNO <sub>2</sub>                    | Observation            | % NaNO <sub>2</sub>                  | Observation                                   |
| Oil phase I  | 19.8                                   | Unstable               | 23.2%                                | Stable microemulsion<br>(viscosity ~ 100 cps) |
|              | 23.6                                   | Unstable               |                                      |   |
| Oil phase IV | 14.3                                   | Unstable               | 16.4                                 | Unstable                                      |
|              | 23.0                                   | Unstable               | 21.1                                 | Unstable                                      |
| Series L     | DEtOHAN and NaNO <sub>2</sub> in water |                        | DEEAN and NaNO <sub>2</sub> in water |   |
|              | % NaNO <sub>2</sub>                    | Observation            | % NaNO <sub>2</sub>                  | Observation                                   |
| Oil phase I  | 23.2                                   | Stable microemulsion   |                                      | Unstable                                      |
| Oil phase IV |  | Unstable               |                                      | Unstable                                      |
|              |  | (viscosity is 300 cps) | 23.0                                 | Unstable                                      |

All the samples of Series K were unstable. The two feasible samples were oil phase I together with pure DEEAN, and oil phase I together with DEtOHAN and NaNO<sub>2</sub> in water (L). Enough of these two samples were mixed to be able to measure the viscosity. The results are shown in Table 4.6 as well as on Figure 4.4. The viscosity is very low. These results are very promising considering the nitrite content and the fact that the microemulsions did not phase-separate up to that point.

The maximum percentages of NaNO<sub>2</sub> achieved are summarised in Table 4.7 below. The percentages can also be read off Figure 4.4, just before the viscosity peaks.

**Table 4.7: Maximum percentages of NaNO<sub>2</sub> achieved in the experiments**

| Series | Oil phase | Water phase                            | % NaNO <sub>2</sub> achieved |
|--------|-----------|--|------------------------------|
| A      | I         | 5% NaNO <sub>2</sub> in water          | 1 – 2%                       |
| B      | I         | 20% NaNO <sub>2</sub> in water         | 5 – 6%                       |
| C      | I         | 35% NaNO <sub>2</sub> in water         | 10 – 12%                     |
| G      | X         | 30% NaNO <sub>2</sub> in water         | 10 – 11%                     |
| H      | I         | Pure DEEAN                             | 23%                          |
| L      | I         | DEtOHAN and NaNO <sub>2</sub> in water | 23%                          |

For a water phase of only  $\text{NaNO}_2$  in water, the best results were achieved with the 30%  $\text{NaNO}_2$  solution. Overall, the best results were achieved with the amine nitrite salts.

Considering costs, the water phase, which is a mixture of DEtOHAN and  $\text{NaNO}_2$  in water, is superior to the pure amine nitrite. Depending on which water phase was being used, either oil phase X or I gives best results.

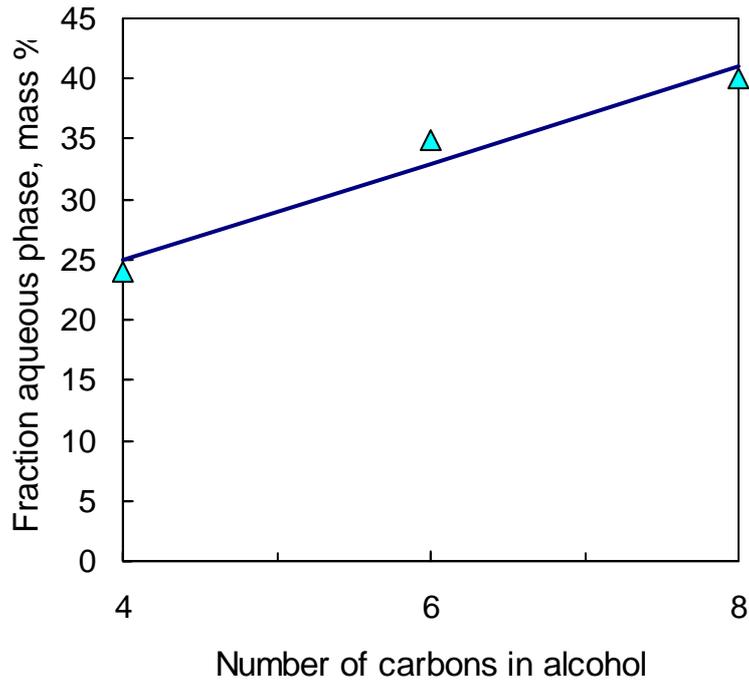
#### 4.2 Preparation of w/o microemulsion containing diethanolamine sulphate using the Atpol oil Phase

A series of concentrations of amine sulphate were prepared and used to make w/o microemulsions with the Atpol oil phase. At all concentrations butanol was used as cosurfactant, except at 4.0 mol/L where hexanol and octanol were also studied. Table 4.8 below shows the maximum amounts of aqueous phase solubilized in microemulsion for each concentration.

It can be seen from the table that the aqueous phase tolerated by the microemulsion in this case increases linearly with the concentration. The following plot (Figure 4.8) details the microemulsion region for each concentration of amine sulphate and the maximum amounts of aqueous phase that can be tolerated by the microemulsion system.

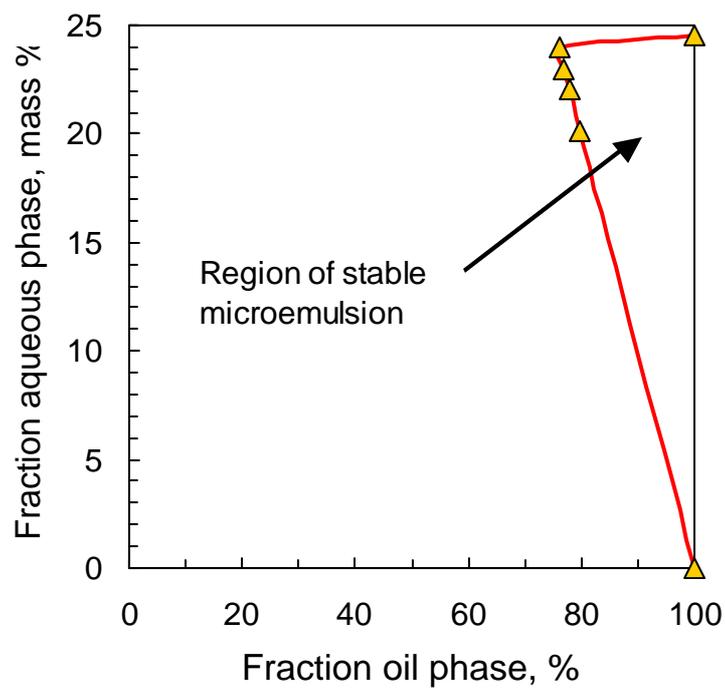
**Table 4.8: Maximum amounts of aqueous phase solubilized in microemulsion for diethanolamine sulphate**

| Concentration (mol/L)     | Oil phase in microemulsion (g) | Aqueous phase in microemulsion (g) | % Oil phase in microemulsion | % Aqueous phase in microemulsion |
|---------------------------|--------------------------------|------------------------------------|------------------------------|----------------------------------|
| 0.125                     | 8.6                            | 1.39                               | 86.09                        | 13.91                            |
| 0.25                      | 8.62                           | 1.4                                | 86.03                        | 13.97                            |
| 0.5                       | 8.6                            | 1.42                               | 85.83                        | 14.17                            |
| 1.0                       | 8.55                           | 1.45                               | 85.50                        | 14.50                            |
| 2.0                       | 8.11                           | 1.91                               | 80.94                        | 19.06                            |
| 4.0                       | 7.61                           | 2.4                                | 76.02                        | 23.98                            |
| 4.0 ( <i>in hexanol</i> ) | 6.51                           | 3.49                               | 65.10                        | 34.90                            |
| 4.0 ( <i>in octanol</i> ) | 6.01                           | 4.01                               | 59.98                        | 40.02                            |



**Figure 4.8: Effect of cosurfactant chain length on the maximum amounts of 4M aqueous diethanolamine sulphate emulsified by Atpol E3205**

Figure 4.9 shows the microemulsion region and maximum amount of 4.0 M amine sulphate solution tolerated by the microemulsion system stabilised by ATPOL.



**Figure 4.9: Microemulsion phase diagram: Emulsifying 4.0 M diethanolamine sulphate**

Figure 4.10 details the phase-separation point for w/o microemulsion with 2.0 M amine sulphate containing butanol as cosurfactant.

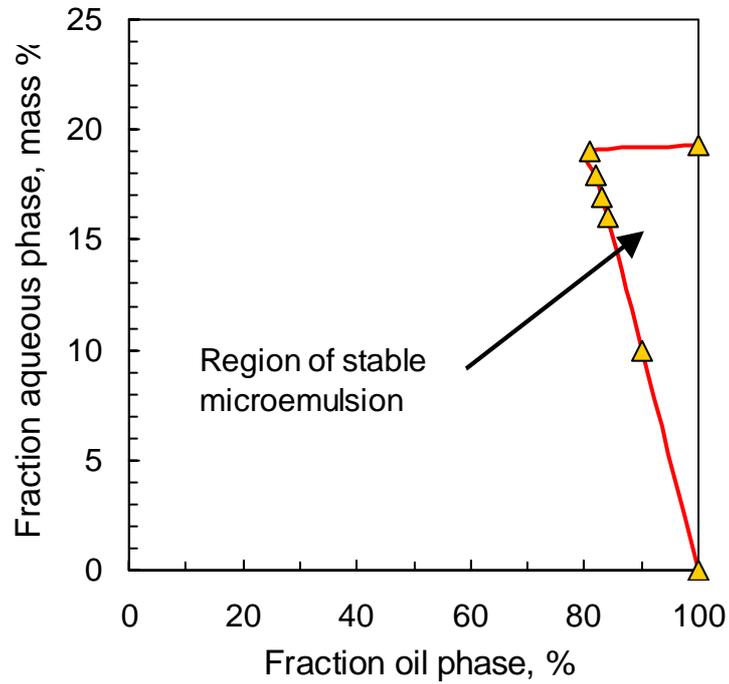


Figure 4.10: Microemulsion phase diagram: Emulsifying 2.0 M diethanolamine sulphate

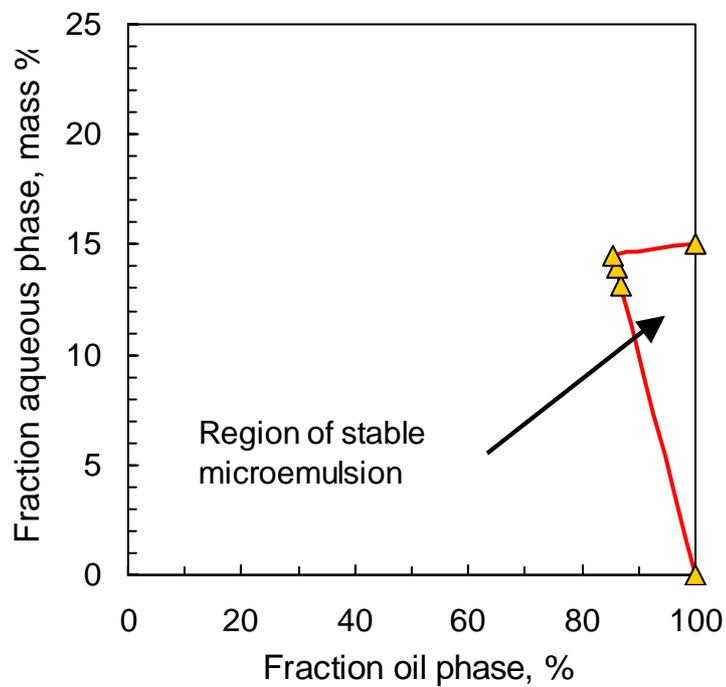
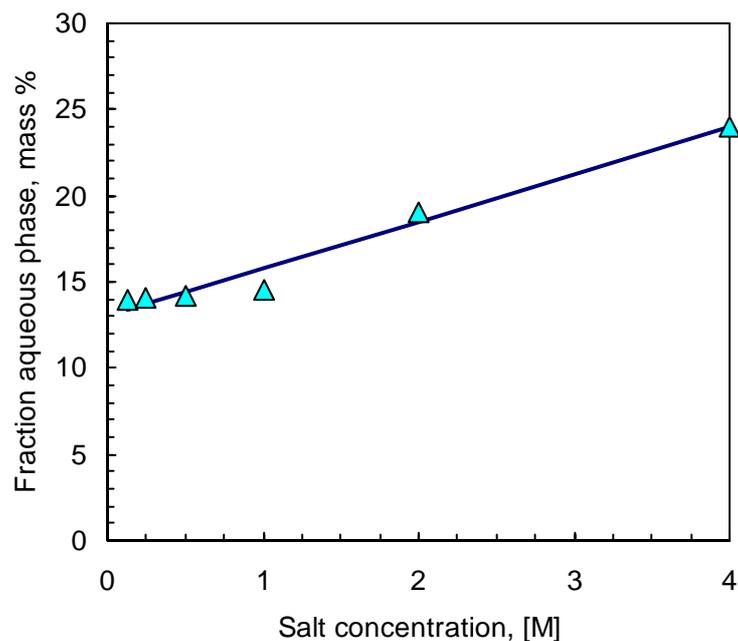


Figure 4.11: Microemulsion phase diagram: Emulsifying 1.0 M diethanolamine sulphate



**Figure 4.12: Maximum amounts of aqueous diethanolamine sulphate emulsified in a w/o microemulsion stabilised by Atpol E3205**

The effect of alcohol chain length or type of cosurfactant was studied for 4.0 M amine sulphate and 0.125 M amine sulphate. However, at a concentration of 4.0 M, the effect of the cosurfactant chain length is more pronounced. This implies that as the chain length of the alcohol is increased, the partitioning of the cosurfactant is enhanced for ATPOL surfactant and hence the curvature of the surfactant is enhanced.

Figure 4.8 illustrates the effect of alcohol chain length on the microemulsion system at 4.0 M amine sulphate. From the phase diagrams it can be seen that the amount of aqueous phase solubilized in the microemulsion increase with ionic strength to a certain point, and beyond that point, no microemulsion can be formed.

#### **4.3 Preparation of w/o microemulsion containing diethanolamine phosphate using the Atpol oil phase**

A similar experimental set-up to diethanolamine sulphate for making a w/o microemulsion was also investigated for diethanolamine phosphate. In the microemulsion system, butanol was used as a cosurfactant for all concentrations. Hexanol and octanol were used as cosurfactants only for the 4.0 M concentration, whilst maintaining same number of moles of

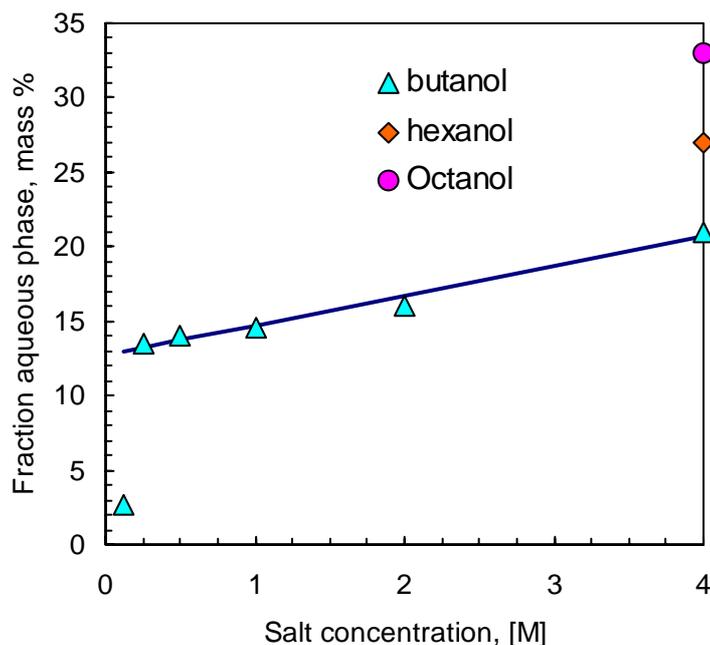
alcohol in the microemulsion. Table 4.9 below shows the maximum amounts of aqueous phase solubilization in microemulsion for each concentration.

**Table 4.9: Maximum amounts of aqueous phase in microemulsion for diethanolamine phosphate**

| <b>Concentration<br/>(mol/L)</b> | <b>Oil phase in<br/>microemulsion<br/>(g)</b> | <b>Aqueous phase in<br/>microemulsion<br/>(g)</b> | <b>% oil phase in<br/>microemulsion</b> | <b>% Aqueous<br/>phase in<br/>microemulsion</b> |
|----------------------------------|---|---|---|---|
| 0.125                            | 17.30   | 2.71  | 86.46                                   | 13.54   |
| 0.25                             | 17.30   | 2.70  | 86.50                                   | 13.50   |
| 0.5                              | 8.71  | 1.32  | 86.84                                   | 13.16   |
| 1.0                              | 8.54  | 1.45  | 85.49                                   | 14.51   |
| 2.0                              | 16.81   | 3.22  | 83.92                                   | 16.08   |
| 4.0                              | 7.91  | 2.10  | 79.02                                   | 20.98   |
| 4 ( <i>in hexanol</i> )          | 7.30  | 2.69  | 73.07                                   | 26.93   |
| 4 ( <i>in octanol</i> )          | 6.71  | 3.30  | 67.03                                   | 32.97   |

The details in the table above are summarised in figure 4.13.

The same trend observed for the w/o microemulsion with amine sulphate is also observed for diethanolamine phosphate. Microemulsion emulsification in this system increases with concentration. However, the difference between the two systems is that the maximum amount of diethanolamine phosphate aqueous phase emulsification for each concentration is less than that for amine sulphate. For instance at 4.0 M, the maximum amount of aqueous phase emulsified for diethanolamine sulphate is ~24%, whereas for diethanolamine phosphate it is ~21%.

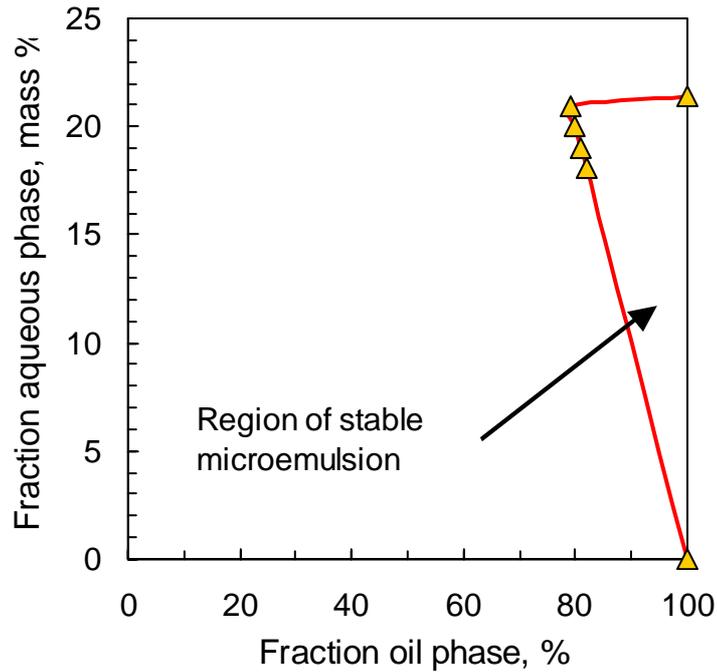


**Figure 4.13: Maximum amounts of aqueous diethanolamine phosphate emulsified in a w/o microemulsion stabilised by Atpol E3205**

The effect of alcohol chain length also resembles the effect of the amine sulphate system. As the chain length increases, the solubilization of the aqueous phase is enhanced. This could be due to the high polarity of the alcohol that is more compatible with oil as the chain length is increased, coupled with enhanced partitioning of the alcohol in the surfactant system.

This probably leads to even better curvature of the surfactant, which result in increased emulsification of even more aqueous phase.

From Table 4.9, it can be seen that the maximum amount of diethanolamine phosphate aqueous phase solubilization in the w/o microemulsion is ~ 21%, with butanol as cosurfactant. Above this point, phase separation of the microemulsion occurs. Figure 4.14 illustrates the point at which phase separation occurs for 4.0 M diethanolamine phosphate.

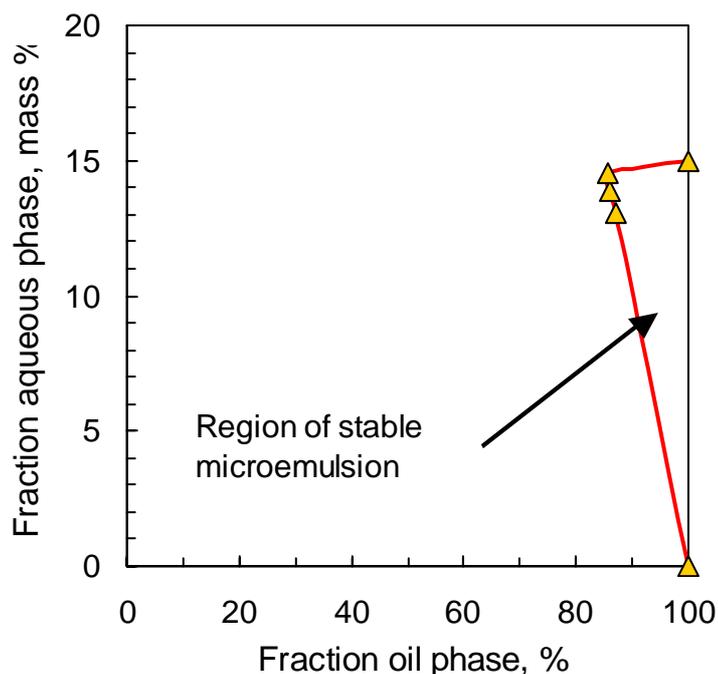


**Figure 4.14: Microemulsion phase diagram: Emulsifying 4 M diethanolamine phosphate**

The phase diagram shows the region of stable microemulsion.

The results for both the amine sulphate and diethanolamine phosphate systems clearly show that there is a critical or optimum ionic strength at which the aqueous phase solubilization in the microemulsion is highest for each concentration. The ionic strength of 2.0 M amine sulphate is less than that of diethanolamine phosphate at the same concentration. This is obviously due to the difference in charge number of the sulphate and phosphate. From the data, it can be deduced that aqueous phase solubilization increases with concentration/ionic strength and increases with the polarity/chain length of the cosurfactant (alcohol). However, comparing the data for amine sulphate and diethanolamine phosphate, it can be seen that the solubilization is higher with amine sulphate salt, although amine sulphate has lower ionic strength compared with diethanolamine phosphate. This confirms that there is an optimum ionic strength at which solubilization is at maximum.

Figures 4.15 details the emulsification behaviour of diethanolamine phosphate at 1.0 mol/l.



**Figure 4.15: Microemulsion phase diagram: Emulsifying 1 M diethanolamine phosphate**

The effect of ionic strength is more pronounced in the 0.5 M concentration; below this concentration emulsification seems to be constant. In this study, the overall results for the Atpol system show that better solubilization/emulsification in the w/o microemulsion is achieved with diethanolamine sulphate, with hexanol as a cosurfactant.

#### **4.4 Preparation of w/o microemulsion stabilised by didodecyldimethyl ammonium chloride (DDAC)**

The effect of ionic strength in the DDAC system was studied for ammonium acetate, sodium acetate, magnesium acetate and zinc acetate. A series of different concentrations of each salt were prepared and used to make w/o microemulsions with Quat oil phase. The oil phase of the w/o microemulsion was made of an alcohol, DDAC and Shellsol 2325 oil. At all the different concentrations butanol, hexanol and octanol were used as cosurfactant.

Table 4.10 shows the highest amounts of aqueous phase that can be tolerated by the resulting microemulsion for ammonium acetate, with butanol as cosurfactant.

**Table 4.10: Maximum amounts of aqueous phase in the microemulsion containing ammonium acetate and the oil phase with butanol**

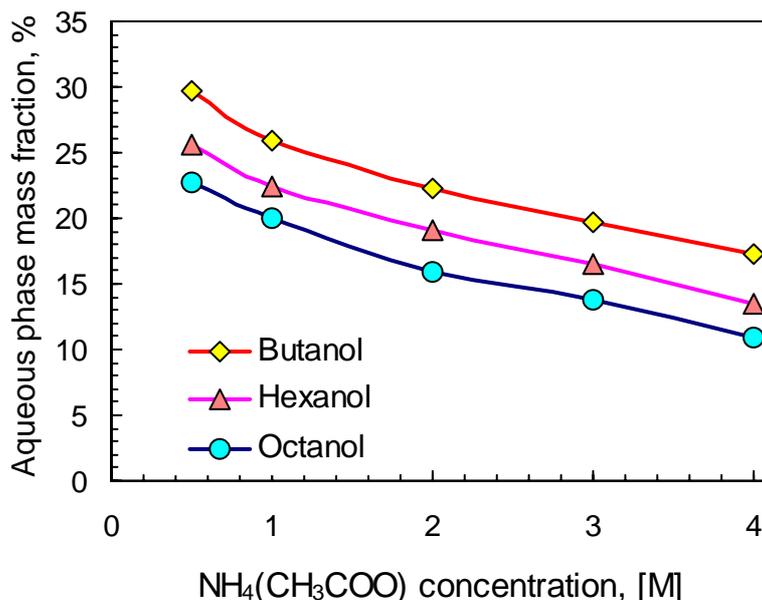
| Concentration (mol/L) | % Oil phase | % Water phase |
|-----------------------|-------------|---------------|
| 0.5                   | 70.23       | 29.77         |
| 1.0                   | 74.14       | 25.86         |
| 2.0                   | 77.72       | 22.28         |
| 3.0                   | 80.32       | 19.68         |
| 4.0                   | 82.69       | 17.31         |

Figure 4.16 shows the solubilization behaviour of the aqueous phase in the DDAC system containing ammonium acetate as aqueous phase. From Figure 4.16 it can be seen that the maximum aqueous phase is solubilization at 0.5 M ammonium acetate. The plot shows that for the DDAC system studied in this project, solubilization is inversely proportional to ionic strength.

**Table 4.11: Effect of substituting butanol with hexanol in the ammonium acetate w/o microemulsion stabilised by DDAC**

| Concentration (mol/L) | % Oil phase | % Aqueous phase |
|-----------------------|-------------|-----------------|
| 0.5                   | 74.38       | 25.62           |
| 1.0                   | 77.64       | 22.36           |
| 2.0                   | 80.91       | 19.09           |
| 3.0                   | 83.56       | 16.44           |
| 4.0                   | 86.51       | 13.49           |

Table 4.11 details the amount of ammonium acetate tolerated by the DDAC w/o microemulsion with hexanol as cosurfactant. It shows that increasing the alcohol chain length leads to reduced solubilization for the DDAC system. This could be due to the cationic nature of the surfactant, which is not perfectly compatible with longer-chain alcohols other than butanol. This behaviour is explained in many publications in which short-chain alcohols have been successfully used as cosurfactants, specifically for cationic surfactants.



**Figure 4.16: Aqueous phase solubilization by w/o microemulsion containing ammonium acetate with different cosurfactants**

From Figures 4.16 and 4.17 it can be seen that the amount of water phase in the microemulsion decreases with an increase in the alcohol chain length. This could be attributed to the long chain of the cosurfactant, which might be reducing the curvature of the micelles and hence reducing the amount of aqueous phase that can be tolerated by the microemulsion. Watt *et al* also reported that butanol yields better emulsification in microemulsion system stabilized by cationic surfactant, cetyltrimethylammonium chloride.

Table 4.12 below shows the aqueous phase solubilization for sodium acetate. It can be seen that the aqueous phase uptake in the microemulsion has been reduced by comparison with ammonium acetate.

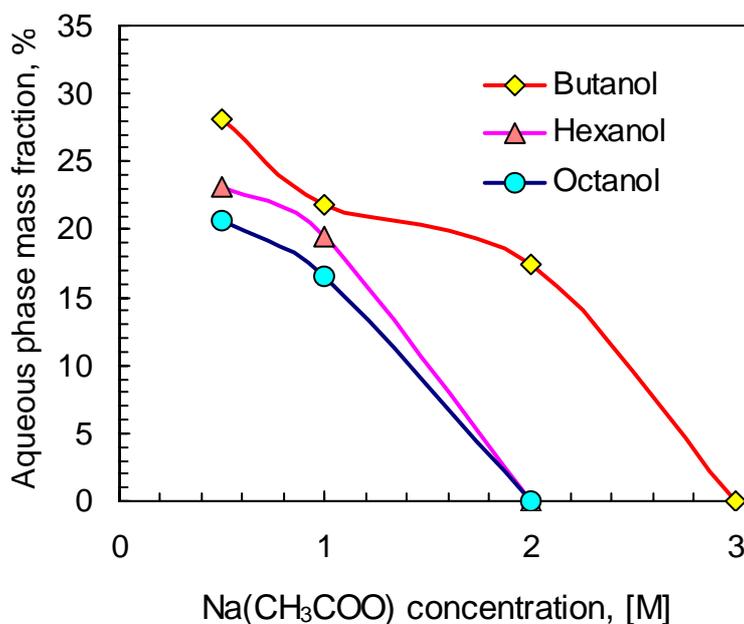
**Table 4.12: Solubilization of sodium acetate in the DDAC system with butanol**

| Concentration (mol/L) | % Oil phase | % Aqueous phase |
|-----------------------|-------------|-----------------|
| 0.5                   | 71.84       | 28.16           |
| 1.0                   | 78.12       | 21.88           |
| 2.0                   | 82.51       | 17.49           |
| 3.0                   | 100.00      | 0.00            |

Table 4.13 and Figure 4.17 show the amount of sodium acetate solubilization in the w/o microemulsion stabilised by DDAC in the presence of hexanol. The solubilization has been reduced by over 60% compared with the system in which butanol acts as a cosurfactant in the DDAC system.

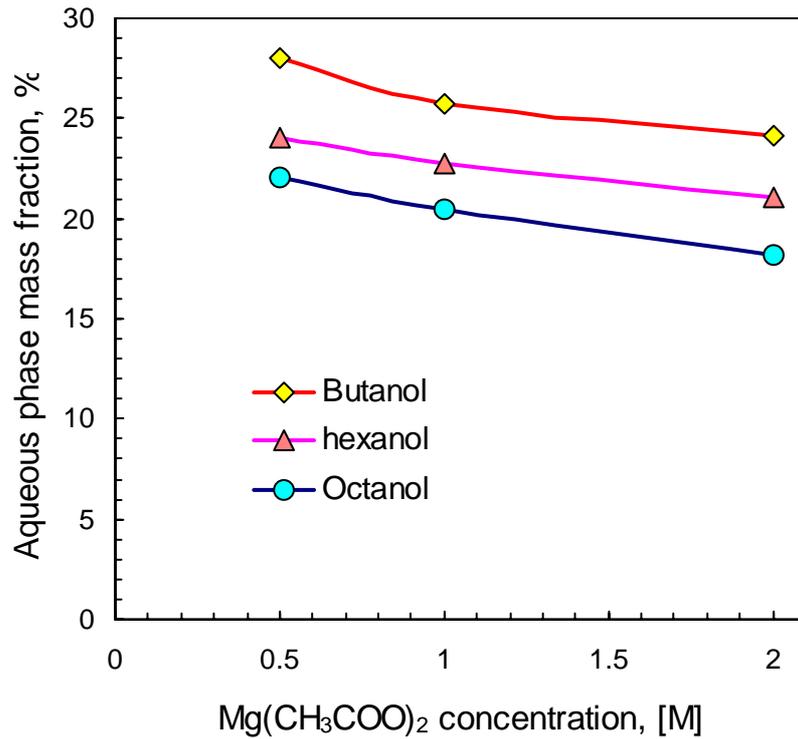
**Table 4.13: Amounts of sodium acetate in the w/o microemulsion at different concentrations with hexanol as a cosurfactant**

| Concentration (mol/L) | % Oil phase | % Aqueous phase |
|-----------------------|-------------|-----------------|
| 0.5                   | 76.85       | 23.15           |
| 1.0                   | 80.58       | 19.42           |
| 2.0                   | 100.00      | 0.00            |

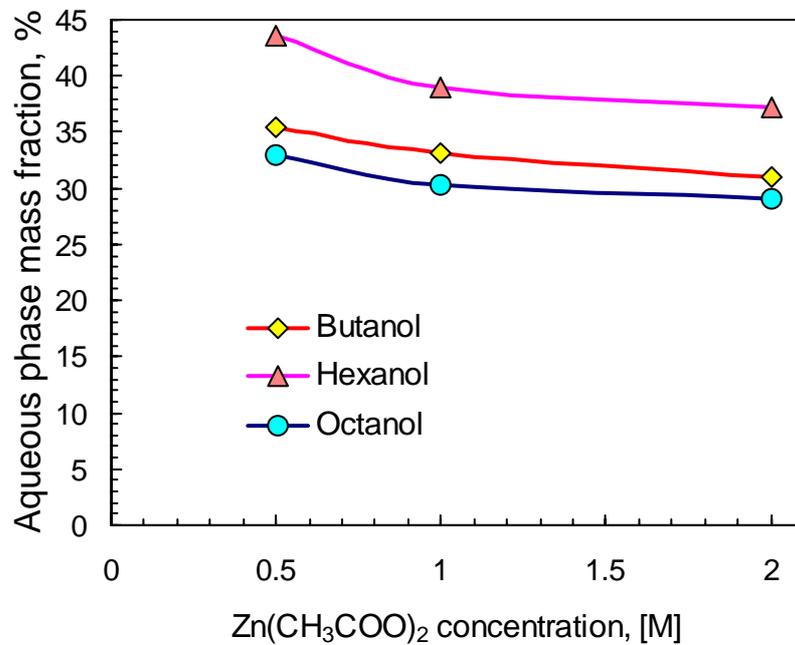


**Figure 4.17: Maximum amounts of sodium acetate solubilization by the DDAC w/o microemulsion with different cosurfactants**

The results also confirm that increasing the alcohol chain length for this system leads to reduced solubilization of the aqueous phase for the DDAC system. Figure 4.17 details that as the concentration of the aqueous phase is increased, the amount of sodium acetate tolerated by the DDAC microemulsion system is reduced. This indicates that very high ionic strength in the DDAC system leads to reduced solubilization.



**Figure 4.18: Maximum amounts of magnesium acetate solubilization by the DDAC w/o microemulsion with different cosurfactants**



**Figure 4.19: Effects of salinity and cosurfactant in the w/o microemulsion stabilised by DDAC, with zinc acetate as the aqueous phase**

## 5. CONCLUSION

The aim of this project was to investigate factors that influence the aqueous phase uptake in w/o microemulsions for two systems, i.e. the ATPOL and Quat systems. For this reason the effects of ionic strength and cosurfactants were the main points of focus for this project. It must be emphasised that no publications dealing with the use of nonylphenol ethoxylated phosphate ester in microemulsions were found in available literature. However, information on didodecyltrimethylammonium chloride (DDAC) in microemulsions has been published in many articles. In most w/o microemulsion formulations in practice and as described in the literature, the amount of aqueous phase in the microemulsion is usually less than 40%.

### 5.1 Preparation of w/o microemulsion with amine nitrite stabilised by Atpol

Nitrite ions decompose to form nitrogen in an acidic medium and thus the nitrite can be used as a source of nitrogen gas for some applications, such as emulsion explosives. The aim for this project was to make a w/o microemulsion containing at least 23% nitrite in the dispersed phase. For an aqueous phase of only  $\text{NaNO}_2$  in water, the best results were achieved with the 30%  $\text{NaNO}_2$  solution. Overall, the best results were achieved with the amine nitrite salts.

Considering costs, the aqueous phase, which is a mixture of DEtOHAN and  $\text{NaNO}_2$  in water, is superior to the pure amine nitrite. Of all the surfactants tested in this study, ATPOL gave the best results in terms of making stable microemulsions with higher aqueous phases. However, the amine nitrite salts cannot act on the interface between the water and oil phases.

- The best miscibility was achieved with a mixture of DEEAN and DBAN.

Though the amine nitrite salts cannot replace the surfactant, the water-soluble ones provide a good source of amine nitrite salts in the water phase.

Of all the experiments done to investigate the nitrite content of microemulsions, the highest nitrite contents achieved were:

- About 10% for the ATPOL oil phase and water phase of 30%  $\text{NaNO}_2$  solution.
- 23% for pure DEEAN in the standard ATPOL E 3202 oil phase.

- 23% for a mixture of DEtOHAN and NaNO<sub>2</sub> in water (molar ratio of 1 mole DEtOHAN to 1 mole of NaNO<sub>2</sub> to 6 moles of water) in the standard ATPOL E 3202 oil phase.
- With the same water phase, further experiments should yield valuable information about the effect of the oil-phase mixing ratio on the microemulsion: An increase and decrease in the amount of solvent (Shellsol) used.

## **5.2 Preparation of w/o microemulsion with diethanolamine sulphate and diethanolamine phosphate stabilised by Atpol**

From the results it can be concluded that the aqueous phase solubilization in a w/o microemulsion is dependent on the ionic strength and type of the cosurfactant. Very low and very high ionic strengths yield a low aqueous phase. It is recommended that a solution of intermediate ionic strength be used for the best results. For the ATPOL system, an increase in the chain length of the alcohol and in ionic strength leads to enhanced water-phase solubilization. The increase in solubilization due to the increase in ionic strength can be explained as follows: Diethanolamine salt has lower polarity than water; an increase in the diethanolamine salt concentration means a decrease in the polarity of the aqueous phase. Thus the w/o microemulsion system can tolerate more diethanolamine salt because is better miscible/soluble in oil as opposed to pure water.

According to Attwood and Florence (1983), the formation of a microemulsion is encouraged by the addition of a co-solubilizer, such as a long-chain alcohol, possibly because of the geometric requirements for appropriate curvature in the interfacial region (Sherman, 1968).

## **5.3 Preparation of w/o microemulsion with acetate salts using DDAC as surfactant**

In this study the effect of ionic strength proved to play a vital role in the formulation of the w/o microemulsion. At very high ionic strength, reduced solubilization was observed for all salts. However, the effect of alcohol chain was the opposite of what was observed in the ATPOL system. It was observed that increasing chain length leads to reduced aqueous phase uptake by the w/o microemulsion for all acetate salts. It is recommended that a short-chain alcohol be used as cosurfactant with a cationic surfactant such as DDAC. The investigation of

propyl alcohol and isopropanol could give valuable information with regard to the type of cosurfactant that can be used in a Quat system.

The difference brought about by the type of cosurfactant used for the Atpol and DDAC/Quat systems could be due to the nature of the two surfactants. Atpol is an anionic surfactant with a mixture of single chain (~40%), double chains (~50%) and triple chains (~10%). DDAC is a twin-chain cationic surfactant.

#### **5.4. FINAL CONCLUSION**

From the study it can be concluded that the ionic strength of the aqueous phase, the type of cosurfactant used and the nature of the surfactant play vital roles in the stability and emulsification of water-in-oil (w/o) microemulsions. The two systems of w/o microemulsion stabilised by the anionic surfactant (nonyl phenol phosphate) and the cationic surfactant (didodecyldimethyl ammonium chloride) showed different behaviour in terms of solubilization/emulsification. The first w/o microemulsion system investigated, nonylphenol ethoxylated phosphate ester (ATPOL), showed an increase in solubilization as the cosurfactant chain length increased. This is possibly because of the geometric requirements of the cosurfactant for the appropriate curvature in the interfacial region. It is therefore recommended for this system that a cosurfactant with a medium to long chain length be used to achieve the highest aqueous phase solubilization.

The second microemulsion system was made up of double-chain Quat surfactants, namely 80% didodecyldimethyl ammonium chloride (DDAC), Shellsol oil and an alcohol. In the DDAC system, an increase in the alcohol chain length led to reduced aqueous phase uptake. This can be supported by lots of available literature which confirms that many cationic systems were made using short chain alcohols, predominately butanol. In order to maximise aqueous phase uptake in w/o microemulsions, it is recommended that the polarity of the aqueous phase be reduced, for instance by using oil-soluble-based salts, such as amines. For each system it was found that there is an optimum ionic strength at which aqueous phase uptake is maximised. Beyond that particular ionic strength, microemulsion cannot be formed.

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## 7. APPENDIX: IONIC STRENGTH OF SALTS

Appendix A illustrates the difference in ionic strength of some salts used in this study. The effect of ionic strength is one of the parameters that were investigated.

**APPENDIX A: Ionic strength ( $I = 0.5 \sum C_i z_i^2$ ) of various salts**

| Type of salt      | Molarity/ example  | 4  | 2  | 1 | 0,5 | 0,25 | 0,125 |
|-------------------|--|----|----|---|-----|------|-------|
| <b>1:1</b>        | amine nitrate, sodium acetate, ammonium acetate          | 4  | 2  | 1 | 0,5 | 0,25 | 0,125 |
| <b>1:2 or 2:1</b> | Diethanolamine sulphate, magnesium acetate, zinc acetate | 12 | 6  | 3 | 1,5 | 0,75 | 0,375 |
| <b>1:3</b>        | Diethanolamine phosphate                                 | 24 | 12 | 6 | 3   | 1,5  | 0,75  |