Non-aqueous Microemulsions of Low Dielectric Systems

by

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Abstract

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A theoretical classification for microemulsion systems has been proposed and the broader area of non-aqueous and low dielectric systems for microemulsion study have been identified. The existence of non-aqueous microemulsions in low dielectric media has been demonstrated with ethanol/*n*-hexadecane model systems. The formation, confirmation, types, structures, and properties of such systems have been systematically investigated. Especially, the formation and structures of the interface created by the series of amphiphiles we found has been studied with monolayer, NMR, fluorescence probe and molecular mechanics computer modeling techniques. The knowledge obtained here can be used for the microemulsion study of other non-aqueous and low dielectric systems and applied to theoretical and practical problems.

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Chapter 1

General Introduction

1.1 Microemulsions in General

Microemulsions are thermodynamically stable, multi-component, transparent liquid systems. They usually consist of four major components, with one being non-polar and lipophilic (oil), another being polar and hydrophilic (water), and the rest being both lipophobic and lipophilic (surfactant and cosurfactant). They form spontaneously during preparation, and show a certain type of microscopic droplet structure (oil-in-water or O/W and water-in-oil or W/O, see Table 1.1.1).

Microemulsions are fundamentally different from solutions (molecular dispersions) because they are micro-structured, which makes them very useful in different ways. Compared with emulsions (macroemulsions), they are more stable and easier to form because their formation is thermodynamically favorable. These systems are more complicated than micellar solutions because there are more components and interactions in the system. Microemulsions are a class of artificially made chemical and material systems and microemulsion studies are of fundamental importance.

In 1943, T. P. Hoar and J. H. Schulman (1) first made such a system when they added medium-length alcohol (hexanol) to the opalescent water/potassium oleate/benzene coarse emulsion; the system cleared spontaneously and became stable and homogeneous. In 1959, Schulman and co-workers (2) proposed the term microemulsion; earlier terms had

Table 1.1.1 Features of Microemulsions

Composition four major components	Water (W) Oil (O), e.g. benzene Surfactant, e.g. potassium oleate Cosurfactant, e.g. hexanol
Structure two types of microdroplets	Oil-in-water (O/W) Water-in-oil (W/O)
Thermodynamics	Stable
Appearance	Optically clear and transparent (diameter of the droplet < 120 nm) Homogeneous appearance
Preparation	Spontaneous formation during titration

included transparent water and oleopathic oil dispersions, hydromicelles, hydropathic oleomicelles, and swelled micelles (3, 4, 5).

After Schulman's pioneering work, numerous studies have been carried out in this interesting and fascinating area. Several theories and models (6, 7, 8, 9, 10) of the formation and structure of microemulsions have been proposed. The focus of extensive research efforts and the progress in the field has been reported regularly and books and monographs on the topics are available (11, 12, 13, 14, 15, 16). Over these years, the concept of microemulsion has spread into many branches of science and engineering and the methodology and principles of microemulsions have been adopted in various applications.

Microemulsions can be classified into three categories according to the nature and composition of the polar solvent, that is, aqueous, hybrid and non-aqueous microemulsions (Table 1.1.2). Although microemulsion studies have been pursued for many years, most of the research was water-related and the models and theories have been based on aqueous systems with water as the polar liquid. There are only a few systems involving non-aqueous solvents. It is necessary and natural to expand the research into the non-aqueous areas.

Table 1.1.2 Microemulsion Classification

Based on the nature and composition of the polar liquid component, microemulsions can be classified as the following types:

I. **Aqueous microemulsions** (normal microemulsions)

II. **Hybrid microemulsions** (polar liquid = solvent + water)

III. **Non-aqueous microemulsions** (polar liquid = pure non-aq solvent)

This classification helps to clarify our thinking on microemulsions because each of these types requires us to adopt specific methodology in the formation and study of these systems.

1.2 Importance of Non-aqueous Systems

Unlike aqueous systems, non-aqueous media are much less studied for microemulsions. Often they have not been studied at all for micellar systems or emulsion systems. Little is known about their behavior or interactions with amphiphiles, or the nature of such systems in the liquid state. Many concepts holding effectively for aqueous systems, such as CMC (critical micellar concentration), may not be true or apply here.

Nevertheless, non-aqueous media cover almost all important solvents except water. They offer theoretical interest and are of practical importance to various industrial fields (Table 1.2.1). For example, many organic reactions can be carried out only or carried out better in non-aqueous solvents. Numerous drugs are only soluble in organic solvents. Studying microemulsion phenomena in non-aqueous media should be of fundamental importance.

Table 1.2.1 Importance of Non-aqueous Systems

----Media for organic reactions

----Media for drug processing and delivery

----Solvents for agricultural chemicals

----Working fluids for refrigeration systems

----Media for inkjet printing

----Precursor and controlling media for nanomaterials

1.3 Work and Efforts for Non-aqueous Microemulsions

1.3.1 General Status of Non-aqueous Microemulsion Studies

Winsor's work was to be the first involved in non-aqueous solvents. In 1948, he reported (17) that replacing the water (dielectric constant, ε=80.2 at 20°C) with glycol (ε=37.7 at 20°C) in a W/O type system (the surfactant being ionic) produces an O/W type system. But using nonionic surfactant, Verzaro et al (18) reported a different behavior. Based on these observations, it is seen that predicting the variation theoretically when water is replaced by other polar solvents is difficult (19). This difficulty is made even more evident when water is replaced by 1,3-propanediol (ε=35 at 20°C) or 1,4-butanediol (20).

The following sections discuss major efforts reported in the literature intended for non-aqueous microemulsions, including hybrid microemulsions, non-aqueous micellar systems and non-aqueous emulsions. Studies on non-aqueous microemulsions have so far been mostly focused on three polar solvents: formamide (ε=106.0 at 20°C), glycerol (ε=42.5 at 20°C) and glycol (ε=37.7 at 20°C) and other diols. Introductory work on non-aqueous microemulsion studies of these three systems all appeared in 1984 and the most successful system was the formamide system. Clearly, all of the polar solvents studied have a dielectric constant larger than 30 and none of the work involved solvents with dielectric constant less than 30. Besides this, most of the studies were carried out under atmospheric pressure and room temperature.

The published work on non-aqueous microemulsions will be summarized in the following.

1.3.2 Formamide Systems

In 1975, Attwood et al (21) observed that addition of a low concentration of formamide or N-methylformamide could enhance the solubilization of water in the center of the Manoxol OT micelle. This could be related to the greater ion-dipole interaction between the mixture solubilized in the micellar core and the sodium ion of the anionic surfactant.

In 1984. Lattes and Rico (22) established the microemulsion monophase region in formamide/cyclohexane/1-butanol/CTAB (cetyltrimethyl ammonium bromide) or CTbPB (cetyltributylphosphonium bromide) system. Typical results showed total surfactant requirements of 40% (by weight) for equal amounts of formamide and hydrocarbon. As is the case for aqueous microemulsions. the microemulsifier to solvent ratio to obtain initial solubilization was very high both for the polar liquid and the oil. Transparency was the criterion for the formation.

The same workers (23) also used the formamide system to obtain a large. continuous monophasic perfluorinated microemulsion region with fluoroalkane using a modest amount of potassium 2,2,3,3-tetrahydroperfluoroundecanoate and 1,1,2,2-tetrahydro-perfluorohexanol at 25°C. Change in electrical conductivity was the evidence against a cosolubilized system and for a microemulsion. An interesting choice of surfactant for micellization in formamide was the fluorinated long chain phosphonium salts which are not soluble in water; the sudden change in surface tension was judged as indicating a critical micellization concentration (24).

Later, they studied chemical reactions in various formamide microemulsions (25, 26, 27, 28, 29, 30, 31). The Diels-Alder reaction (25, 26, 27, 28) between methyl acrylate and cyclopentadiene was carried out to probe surfactant solutions in formamide and discontinuities in reaction selectivity indicated the presence of structured phases. Two

distinct zones in the microemulsion systems have been demonstrated and good selectivity and high yields can be obtained for the reaction. The γ radiolytic amidation of $C_8F_{17}CH=CH_2$ in formamide microemulsions demonstrated the feasibility of carrying out reactions in the bicontinuous subphase (29). The Wacker process (30, 31) has also been studied in formamide microemulsions.

Moreover, they prepared some nonionic microemulsions (27, 28) of formamide/ toluene/isopropanol using Pluronic L-64 and F-88 as surfactants (copolymers of ethylene oxide and propylene oxide). These microemulsions represent valuable media for synthetic purposes such as Diels-Alder reactions and photoamidation of olefins (29, 30, 31).

In 1987, studying the system formamide/cyclohexane/1-butanol/CTAB, they found evidence of micelles and microemulsions using X-ray scattering analysis. The results were related to previous measurements of electrical conductivity (32).

In 1991, they (33) described the aggregation of cationic surfactants dodecylalkyl-dimethylammonium and octylalkyldimethylammonium bromides in formamide and for the first time prepared vesicles from these systems.

While most work on formamide systems was successfully carried out by the Lattes group, other researchers made their own contributions.

In 1988, Friberg and Rong (34), from light-scattering measurements, determined that the system formamide/sodium dodecyl sulfate/hexanol/toluene showed no indications of association structures, and they concluded that these "microemulsions" are in fact non-structured solutions. The tie lines in the 4-component system were "vertically" oriented connecting toluene-rich phases with phases with low content of toluene.

From 1990 to 1992, Duerfler and Borrmeister (35, 36, 37) compared phase regions among different solvents, including formamide for microemulsion formation, using surfactants SDS, CTAB, TX 100 and TX 114.

In 1992, Schubert et al (38) studied the effect of replacing water by formamide in the system water/$C_{12}E_4$/C_8H_{18}. Small-angle neutron scattering (SANS) spectra indicated the existence of droplet and bicontinuous structures.

The formamide systems have been the most successful for the purpose of non-aqueous microemulsions.

1.3.3 Glycerol Systems

In 1969, Peterson (39) showed that the polyols glycerol, propylene glycol and polyethylene glycol 400 could be emulsified with olive oil to make oil-in-polyol emulsions. The order of mixing was important, and anionic emulsifier precursors were best suited for the preparation of stable emulsions.

In 1984, searching for non-aqueous emulsions as drug carriers in gelatin capsules, Bauer et al (40) observed that glycerol and 1,2-propylene glycol showed strong incompatible effects with the gelatins and they could be used only in limited quantities in the formulations. Later, Lyapunov et al (41) studied the effects of non-aqueous solvents on properties of the pharmaceutical emulsions and showed that glycerol had a smaller influence on the stability of the emulsions than polyoxyethylene 400, propylene glycol, ethanol and isopropanol.

In 1984, Fletcher et al (42) carried out the first microemulsion investigation with glycerol. The system consisted of dilute glycerol-in-heptane stabilized by Aerosol OT (AOT, sodium bis(2-ethylhexyl)sulfosuccinate). They found spherical droplets with attractive interactions between them as the stability limit was approached.

In 1987, Friberg and Liang (43) studied phase diagrams for the glycerol-AOT system combination with decanol as well as with the hydrocarbons decane or p-xylene. Comparison with the corresponding aqueous systems showed the glycerol systems to be less ordered. The isotropic solution region was extended toward lower AOT content, showing the importance of the enhanced interactions between the hydrophobic component and glycerol in comparison with that in the aqueous system.

Later, Holmberg et al (44) studied enzymatic glycerolysis of a model triglyceride in hybrid microemulsion systems containing isooctane, AOT, palm oil and a combination of water and glycerol as the polar component. The reaction was very slow in a completely non-aqueous system. Addition of a small amount of water led to an increased rate of glycerolysis in addition to hydrolysis. The molar ratio of water and glycerol to surfactant turned out to be critical.

Recently, Peyrelasse and Boned and coworkers (45, 46, 47) performed a series of studies on the percolation phenomenon in glycerol/AOT/isooctane systems.

All the AOT systems above form glycerol-in-oil type microemulsions and have been the more successful in the sense of non-aqueous microemulsions than glycerol systems using other surfactants, as we will discuss below.

In 1985, Friberg and Wohn (48) performed a microemulsion study for a system of glycerol, p-xylene, triethanolammonium oleate and oleic acid. The system showed long term stability once prepared but failed to form spontaneously.

Friberg et al (29, 30, 31, 32) and Doerfler and Nestler (33) have investigated systems consisting of glycerol, SDS, and hexanol with or without hydrocarbon (decane or p-xylene) by studying critical phenomena (49), FT-NMR self-diffusion (50), SANS (51) and by comparison with aqueous analogs (52, 53). SANS results showed that the system glycerol-SDS-hexanol had an extremely high degree of polydispersity and agreed with the NMR findings, which indicated that these kinds of microemulsions are rather structureless solutions. Comparison with corresponding aqueous microemulsion gave no indication of long lived aggregates.

1.3.4 Glycol and Diol Systems

Besides Winsor and others' work (17-20) on glycol (or diol)/water hybrid microemulsions, research related to these polar solvents has continued.

In 1977, Sharma (54, 55 , 56) prepared benzene-in-glycol emulsions stabilized with sodium dioctylsulfosuccinate and studied their stability by ultracentrifugation. He found that the ultracentrifugal stability of aqueous emulsions was greater than that of non-aqueous emulsions and addition of water to non-aqueous emulsions decreased the rate of separation of benzene from the emulsions and made the emulsions more stable. Sharma (57, 58) also prepared glycol/monochlorobenzene non-aqueous emulsions using polyoxyethylene sorbitan monoleate or Tween 20, Tween 60, and Tween 80 as the emulsifying agent.

In 1984, Friberg and Pozimek carried out the first non-aqueous microemulsion investigation on the system glycol/lecithin/decane (59, 60). They showed that this system was not an extension of the micellar solutions. Turbidity measurements indicated initial particle sizes between 1000 and 1500 Å. Phase separation occurred after 10-28 days; increasing lecithin and glycol concentrations increased the stability. The microemulsion region was narrow, with approximately equal glycol and decane content, the surfactant requirement being approximately 10% by weight. They also studied (61) the solubilization of methanol and long chain alcohols and a hydrocarbon in the non-aqueous lamellar liquid crystal of lecithin and glycol.

In 1988, Gasco et al (62) studied the incorporation of the drug doxorubicin into nanoparticles obtained by polymerization of methyl cyanoacrylate in a non-aqueous microemulsion consisting of glycol, Aerosol OT, BuOH and hexane. Nanoparticles

containing up to 14 % of doxorubicin were obtained. their mean diameter being 146 nm. After 5 hours only 8% of the drug was released *in vitro* by the particles.

In 1990. Friberg and Sun (63) investigated the microemulsion system glycol/SDS/decanol/toluene by determination of solubility regions and of light scattering intensity. The system without hydrocarbons showed a critical point which remained in the system during the addition of toluene. No other indications of association structures were seen and these microemulsions should be considered as solutions with critical behavior.

After the pharmaceutical emulsion works by Bauer et al (64) and by Lyapunov et al (65) on propylene glycol, Geyer and Tuliani disclosed a patent in 1990 (66) on a drug delivery system in which propylene glycol, containing ibuprofen, was mixed with soya lecithin and ethyl palmitate to obtain a microemulsion solution.

In 1990. Martino et al (67) studied the phase behavior of propylene glycol. glycerol. dodecane and alkylpolyglycol ether (CiEj) surfactant four-component system. Surfactant solubility in the polar organic phase (a mixture of glycerol and propylene glycol) decreased when glycerol content was increased. Small-angle x-ray scattering (SAXS) measurements indicated the presence of interfaces. Martino et al also proposed a simple four-component lattice model (68) to reproduce qualitatively the phase behavior of the above non-aqueous microemulsions.

In 1992, Murthy (69) studied aqueous and hybrid microemulsions of propylene glycol/water and paraffins (alkane oils of more than 17 carbons) emulsified by polyoxyethylene surfactants of the Brij, Neodol and LP series. SAXS gave evidence for the presence of microstructures in these solutions above the melting point of the alkanes. Systematic paths to move from aqueous to non-aqueous microemulsions were outlined.

Recently, Doerfler (70, 71) showed the growth of the monophasic region on the triangular diagrams when water was replaced by non-aqueous solvents (formamide, glycol, propylene glycol, 1,3-butylene glycol, glycerol, DMSO, γ-butyrolactone and acetonitrile) in the system hydrocarbon/pentanol/polar solvent emulsified by surfactants SDS, CTAB, Triton X 100 and X 114. Increasing temperature also had the same effect on these systems.

1.4 Objectives/Approach

The initial concept of non-aqueous microemulsions for low dielectric systems came from our earlier work on HFC134a/oil cosolubilization (72) where both the polar phase and the oil are low in dielectric constant (ε=8.4 for HFC134a and ~2 for the oil); still they are extremely difficult to mix with each other.

This miscibility problem may not look obvious at first, because common low dielectric solvents, such as CH_3Cl, are miscible with the oil. But further thinking and experiments showed that is not the case. Table 1.4 showed that the solubility tests of 1,4-dioxane in hydrocarbon oils. We may notice that even though 1,4-dioxane has a very low dielectric constant (ε=2.04 at 20°C) and is soluble with low molecular weight hydrocarbons, it becomes immiscible with the mineral oils as the molecular weight of the oil increases. This hints that the problem is general in low dielectric situations and it may be possible to mix the polar liquid/oil pair through formation of a non-aqueous microemulsion.

Given the fact that the field of non-aqueous microemulsions is much less studied and the existence of the problem identified above, it should be of interest to conduct research on microemulsions with non-aqueous low dielectric media. In this study, we will try to expand microemulsion study into these fields. Our main efforts will focus on the formation process of such microemulsions.

In doing so, we will first consider the following fundamental questions for non-aqueous microemulsion study:

for a given solvent/oil pair,

---Whether it can form microemulsions or not;

---How to make the microemulsion, with specified type and conditions.

Table 1.4 Solubility Tests of 1,4-Dioxane in Various Oils at 25°C

Oil	Result
n-C_7H_{16}	soluble
n-$C_{10}H_{22}$	soluble
n-$C_{14}H_{30}$	soluble
n-$C_{16}H_{34}$	soluble
Paraffin oil, white & light (Saybolt viscosity 125/135)	not soluble
Paraffin oil, white & light (Saybolt viscosity 158)	not soluble
Suniso 1GS, yellow naphthenic oil (viscosity SUS at 100°F 100)	not soluble
LP-250, white naphthenic oil (viscosity SUS at 100°F <100)	not soluble

We will work on model solvent and oil systems and will try to study and understand some important microemulsion-related features (interfacial tension, cosolubilization and emulsion formation) of these systems. Next, we will try to find an operative approach to non-aqueous microemulsions and try to form them effectively. If this could be done, then we will study microemulsion identification and characterize them accordingly. We will also conduct some studies on the structural and property aspects of these systems and relate them to the formation of these non-aqueous microemulsions.

We hope this introductory study will bring people's interest and attention to non-aqueous and low dielectric systems for microemulsions.

1.5 Summary

In this chapter, we have classified microemulsions into three categories: aqueous, hybrid, and non-aqueous, based on the composition and the nature of the polar solvent, and pointed out the importance of the non-aqueous solvents and their roles in the theoretical and technological development of microemulsions. A literature search and review of the work and efforts to study non-aqueous microemulsions has been given using the dielectric constants of the polar solvent as the criterion. We have also identified the miscibility problem in low dielectric systems and their possibility to form microemulsions. Finally, we have set our objectives and planned our approaches for the study of non-aqueous microemulsions of low dielectric systems.

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Chapter 2

Interfacial Tension and Emulsion Formation Studies on CH3CN/Oil Model Systems

2.1 Introduction

This chapter reflects our initial efforts to prepare non-aqueous microemulsions of low dielectric systems. We will use a common organic solvent, acetonitrile (ε=37.0 at 20°C) as a model for the polar liquid and three types of hydrocarbons for the oil. Because the decrease in interfacial tension plays an important role in the formation of microemulsions (1, 2, 3, 4, 5, 6, 7, 8), we first perform an interfacial tension study on various CH_3CN/oil pairs using some new, non-conventional surfactants that we hope will work for the low dielectric systems. In the case of failure with these non-conventional surfactants, we will try to approach the problem from the emulsion direction and identify possible candidates as the microemulsifier to build the interfacial layer from various surfactants available, because we know, from earlier microemulsion work (4, 9), that microemulsions may be formed from the corresponding emulsions with suitable surfactant/cosurfactant . Through these studies, we hope to find a way to cosolubilize effectively acetonitrile and the oil, and more importantly, to form non-aqueous microemulsions from them, so we can pursue identification and structural studies thereafter.

2.2 Experimental

Hydrocarbon oils. The following three types, all provided by Witco Corp.:

White mineral oil:	LP 250
Alkylbenzene oils:	Zerol 150
	Zerol 300
Naphthenic mineral oils:	Suniso 1GS
	Suniso 3GS
	Suniso 4GS

(see Section 2.3.1).

Surfactants for interfacial tension study (specially synthesized by Witco Corp.):

K EX 1038:	KEMESTER EX 1038.
	mixture of esters of carboxylic dimer acids
K EX 1039:	KEMESTER EX 1039
	mixture of pentaerythritol fatty esters
OAN:	KEMAMINE N-989
	mixture of oleic acid nitriles

Surfactants for emulsion formation study:

Various, supplied by corresponding manufacturers (see Appendix)

Interfacial tension measurement:

The device used to measure the interfacial tension between acetonitrile-surfactant solution and each oil is the Rosano ™ surface tensiometer (10), essentially an enhanced 500 mg (98 mN/m) precision balance (see Figure 2.2.1).

A sand-blasted Teflon blade wettable by the oil phase is equilibrated into the acetonitrile phase (Figure 2.2.2a). Since in each case the oil is heavier than acetonitrile, when the bottom of the blade contacts the oil-acetonitrile interface the blade is pulled into

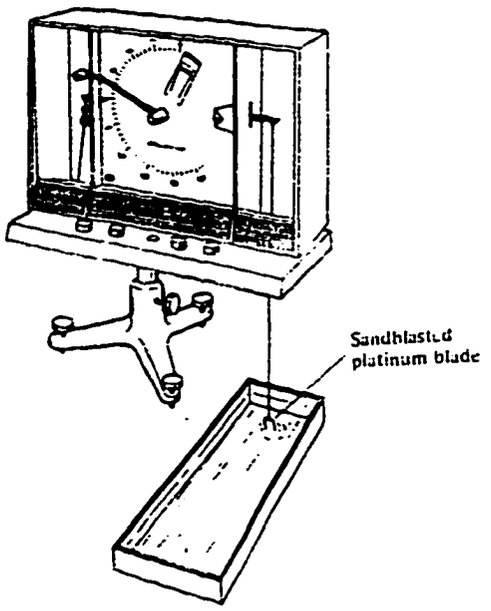

Figure 2.2.1 The Rosano (TM) surface tensiometer.

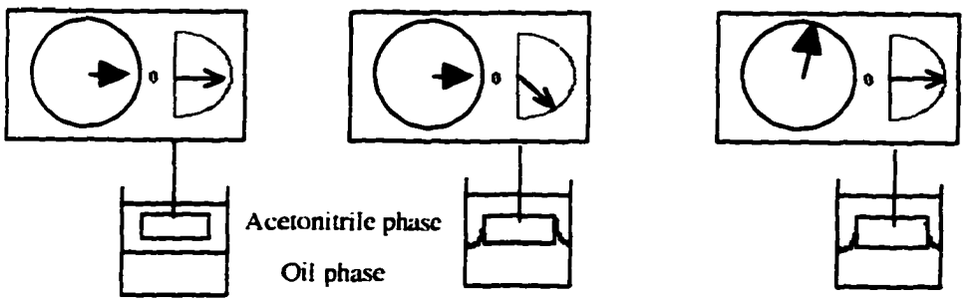

Figure 2.2.2 Procedure for the measurement of the interfacial tension.

the oil phase. The force necessary to bring the bottom of the blade back into the plane of the interface, divided by the perimeter of the blade, yields the value of the interfacial tension (Figures 2.2.2b and 2.2.2c).

The force measured is proportional to the interfacial tension, as shown in the following formula:

$$\textit{Interfacial}\ \text{tension}\ (\text{N/ m}) = \frac{\textit{Force}\ (\text{N})}{\text{Perimeter (m)}} = \frac{\textit{Force}\ (\text{kg})}{\text{Perimeter (m)}} \times 9.80\ \text{kg}^{-1} \cdot \text{N}$$

The perimeter of the blade is 5.10±0.01 cm; the standard deviation for the interfacial tension measurement is about 1%.

Emulsion formation and cosolubilization experiment:

We have tested as many commercial surfactants as possible (approximately 200; see Appendix) for their ability to improve the miscibility/dispersability of hydrocarbon oils in acetonitrile and to form macroemulsions with them. Basically, after 1 g of the surfactant in pure form, 2 mL of acetonitrile, and 2 mL of Z150 oil, are mixed in a test tube, the tube is shaken and inspected visually to observe the degree of mixing or separation. Surfactants which showed any visual dispersion of the hydrocarbon oils in acetonitrile were further studied with the interfacial tension measurements above. Surfactants in aqueous state were vacuum dried before being used.

2.3 Results and Discussions

2.3.1 Interfacial Tension Measurement Results With Mineral Oils

The following tables and graphs show the variation of the interfacial tension between acetonitrile and each oil versus the concentration of the surfactants diluted in acetonitrile. In each case, interfacial tension is measured with the Rosano ™ surface tensiometer.

LP 250 oil

This is a mix of liquid hydrocarbons refined from petroleum. The interfacial tensions between this oil and the acetonitrile phase are shown in Table 2.3.1.1 and plotted versus the concentration of each Witco surfactant in Figure 2.3.1.1.

Zerol 150

This is a mix of alkylbenzenes (benzene, C_{14}-C_{30} alkyl derivatives). The interfacial tensions between this oil and the acetonitrile phase are shown in Table 2.3.1.2 and plotted versus the concentration of each Witco surfactant in Figure 2.3.1.2.

Zerol 300

This is a mix of alkybenzenes. The interfacial tensions between this oil and the acetonitrile phase are shown Table 2.3.1.3 and plotted versus the concentration of each Witco surfactant in Figure 2.3.1.3.

Suniso 1GS oil

This is a hydrotreated light naphthenic petroleum distillate. The interfacial tensions between this oil and the acetonitrile phase are shown in Table 2.3.1.4 and plotted versus the concentration of each Witco surfactant in Figure 2.3.1.4.

Suniso 3GS oil

This is a hydrotreated light naphthenic petroleum distillate. The interfacial tensions between this oil and the acetonitrile phase are shown in Table 2.3.1.5 and plotted versus the concentration of each Witco surfactant in Figure 2.3.1.5.

Suniso 4GS oil

This is a hydrotreated light naphthenic petroleum distillate. The interfacial tensions between this oil and the acetonitrile phase are shown in Table 2.3.1.6 and plotted versus the concentration of each Witco surfactant in Figure 2.3.1.6.

As the tables and figures above indicate, none of the three surfactants tested has a significant effect on the interfacial tension although these surfactants have been specially synthesized for our model system. This forced us to re-think our choice of the microemulsifier, and thus we next made a systematic screening of available commercial and research surfactants.

K EX 1038 γ(mN/m)	K EX 1039 γ(mN/m)	OAN γ(mN/m)	Conc. (g/L)
5.2			200
		6.6	100
7.2	9.2	7.8	10
8.4	9.2	7.6	1
9.4	9.4	7.6	0.1
10.0	9.1		0.01
	10.2		0.001
	10.4		0

Table 2.3.1.1 Interfacial tensions with LP 250 oil.

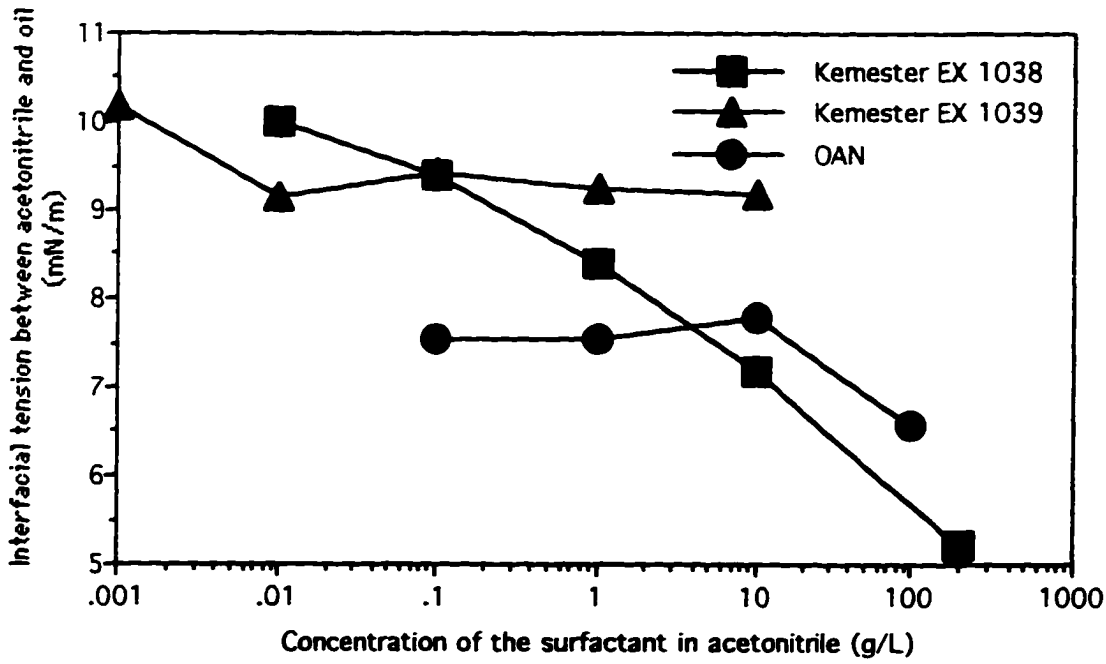

Figure 2.3.1.1 Interfacial tensions with LP 250 oil.

K EX 1038 γ(mN/m)	K EX 1039 γ(mN/m)	OAN γ(mN/m)	Conc. (g/L)
3.5			200
4.2		1.7	100
4.3	4.6	3.	10
4.2	4.6	4.3	1
4.3	4.7	4.8	0.1
4.2	4.9	4.8	0.01
	5.3		0.001
	5.4		0

Table 2.3.1.2 Interfacial tensions with Z150 oil.

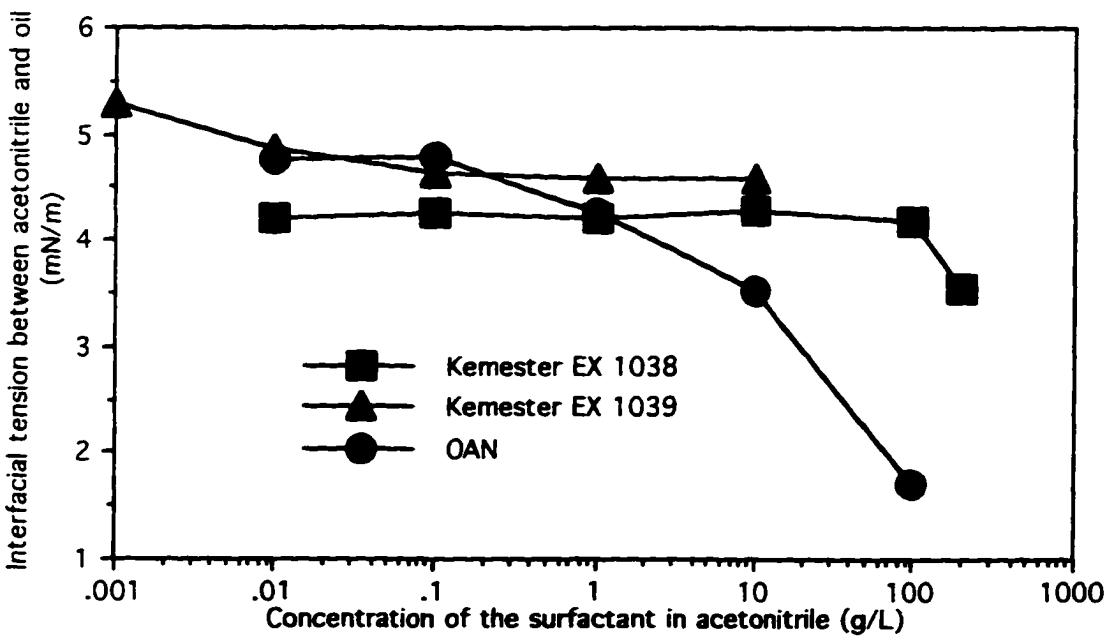

Figure 2.3.1.2 Interfacial tensions with Z150 oil.

K EX 1038 γ(mN/m)	K EX 1039 γ(mN/m)	OAN γ(mN/m)	Conc. (g/L)
1.2			200
3.5		1.5	100
4.1	5.3	4.4	10
4.2	5.4	4.9	1
4.2	5.3	4.9	0.1
4.2	5.2	5.1	0.01
	5.7		0.001
	6.0		0

Table 2.3.1.3 Interfacial tensions with Z300 oil.

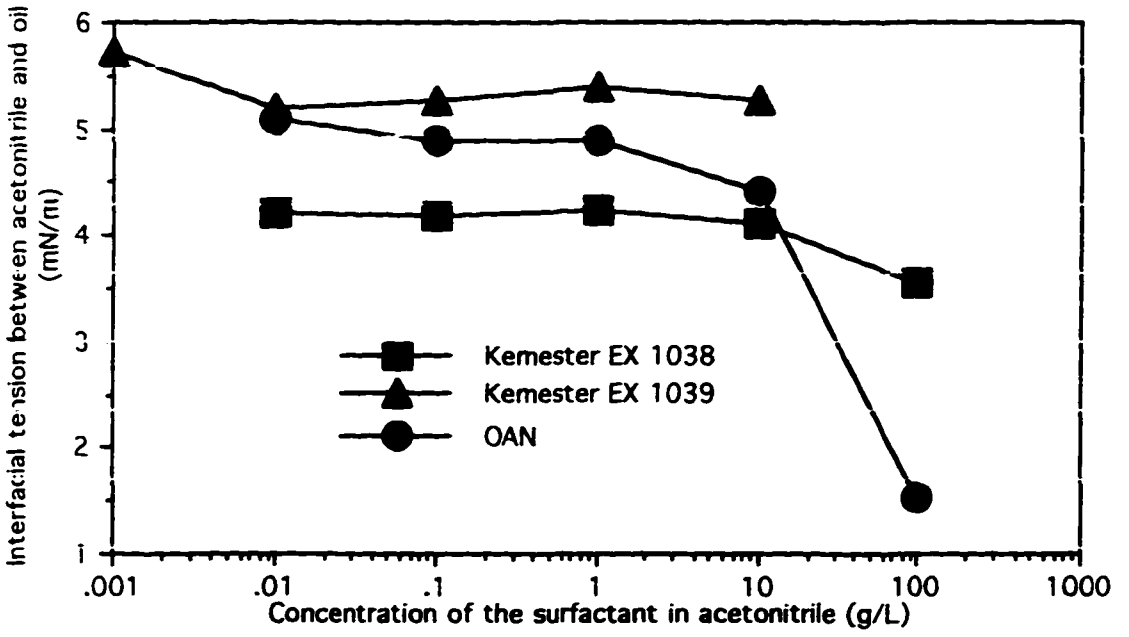

Figure 2.3.1.3 Interfacial tensions with Z300 oil.

K EX 1038 γ(mN/m)	K EX 1039 γ(mN/m)	OAN γ(mN/m)	Conc. (g/L)
3.8			200
4.9		1.8	100
5.9	7.1	6.1	10
6.3	7.1	6.8	1
6.6	7.1	6.7	0.1
6.7	7.1	6.7	0.01
	6.4		0.001
6.5			0

Table 2.3.1.4 Interfacial tensions with 1GS oil.

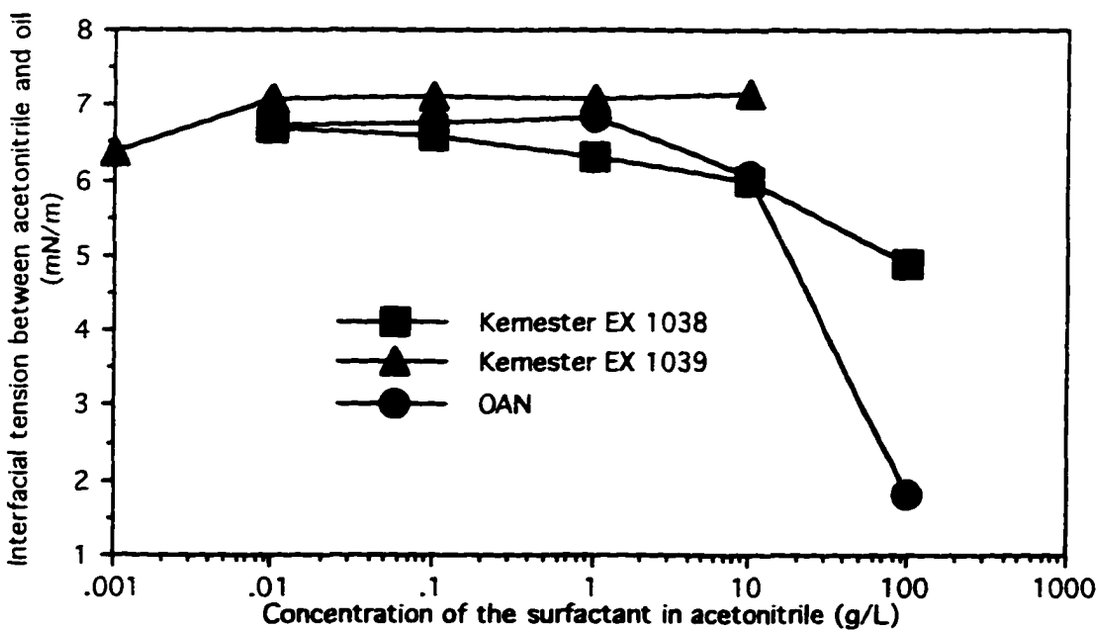

Figure 2.3.1.4 Interfacial tensions with 1GS oil.

K EX 1038 Y(mN/m)	K EX 1039 Y(mN/m)	OAN Y(mN/m)	Conc. (g/L)
3.1			200
3.6		1.9	100
5.5	6.3	5.9	10
6.3	6.5	6.6	1
6.4	6.5	6.6	0.1
6.4	6.5	6.7	0.01
	6.7		0.001
6.8			0

Table 2.3.1.5 Interfacial tensions with 3GS oil.

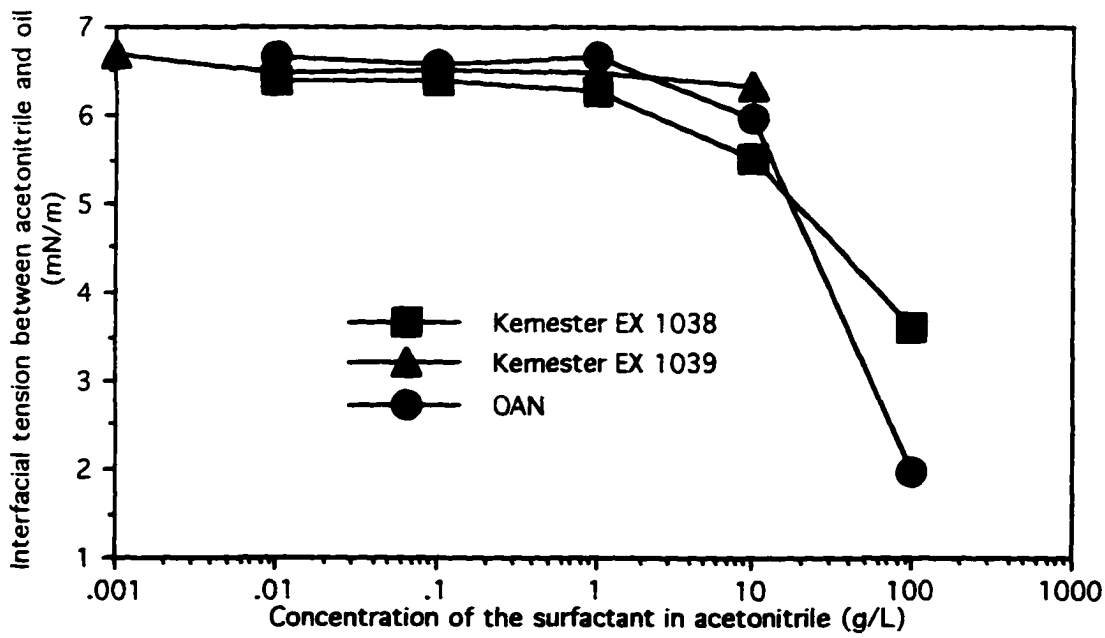

Figure 2.3.1.5 Interfacial tensions with 3GS oil.

K EX 1038 Υ(mN/m)	K EX 1039 Υ(mN/m)	OAN Υ(mN/m)	Conc. (g/L)
3.5			200
4.8		1.7	100
7.1	7.3	6.2	10
7.4	7.3	7.6	1
7.5	7.3	7.4	0.1
7.5	7.3	7.5	0.01
	8.5		0.001
8.7			0

Table 3.3.1.6 Interfacial tensions with 4GS oil.

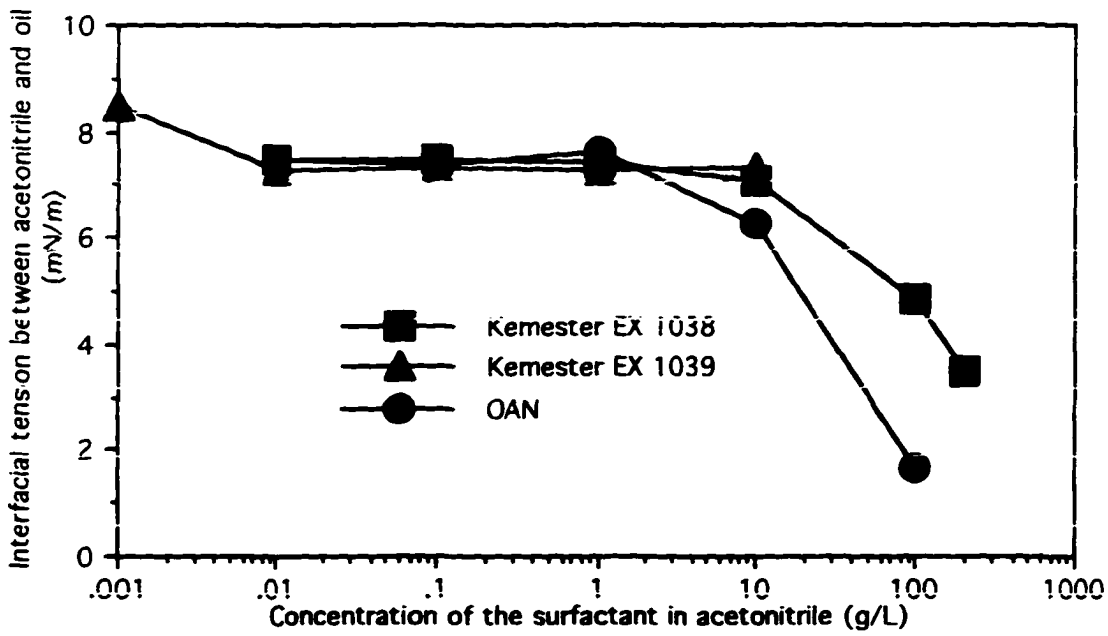

Figure 2.3.1.6 Interfacial tensions with 4GS oil.

2.3.2 Emulsion Formation Test and Interfacial Tension Measurement Results with Commercial and Research Surfactants

To find a suitable microemulsifier for our low dielectric system, we have made a systematic investigation of all the available commercial and research surfactants by examining their ability to form emulsions with acetonitrile/Z150. Most surfactants we tested failed to produce an emulsion; these are listed with their HLB (hydrophile-lipophile balance) values by manufacturers in Appendix 1. This is because they are generally designed for oil/water systems and the difference in dielectric constants between water (ε=81.1) and acetonitrile (ε=37.7) is large.

Only three of the commercial surfactants tested, Polychol 15 Laneth 15, CRODA A 40 and Emulphor EL 620, showed visual dispersibility of the hydrocarbon oils in acetonitrile; they were further studied by the interfacial tension measurement and the results are shown in the following tables and figures.

Surfactants yielding an emulsion:

Polychol 15 Laneth 15

This is an ethoxylated lanolin alcohol (HLB=12.7). Only one oil in each class was tested. The interfacial tensions between these three oils and the acetonitrile phase are shown in Table 2.3.2.1 and plotted versus the concentration of Polychol 15 Laneth 15 surfactant in Figure 2.3.2.1.

CROVOL A 40

This is a polyoxyethylene (20) almond glyceride (HLB=10). Only one oil in each class was tested. The interfacial tensions between these three oils and the acetonitrile phase

are shown in Table 2.3.2.2 and plotted versus the concentration of CROVOL A 40 surfactant in Figure 2.3.2.3.

Emulphor EL 620

This is a polyoxyethylated vegetable oil: Polyoxyethylated (30) castor oil (HLB=12.0). Only one oil in each class was tested. The interfacial tensions between these three oils and the acetonitrile phase are shown in Table 2.3.2.3 and plotted versus the concentration of Emulphor EL 620 surfactant in Figure 2.3.2.3.

The data show that these surfactants only lower the interfacial tension slightly by allowing an interfacial tension of about 2mN/m to be obtained at about 1g/L: they behave similarly to the new Witco surfactants and are no good for the cosolubilization of oil/CH3CN or the formation of non-aqueous microemulsions. One common feature of all these surfactants can be noticed, that is, they all contain a polyoxyethylated chain in their hydrophilic part, as is true of most nonionic surfactants (11, 12, 13).

LP 250 γ(mN/m)	Z150 γ(mN/m)	3GS γ(mN m)	Conc. (g/L)
1.1	0.8	1.0	100
4.5	2.9	3.7	10
9.0	5.3	6.4	1
10.2	5.4	7.5	0.1
10.4	5.4	6.8	0

Table 2.3.2.1 Interfacial tensions for Polychol 15 Laneth 15 surfactant.

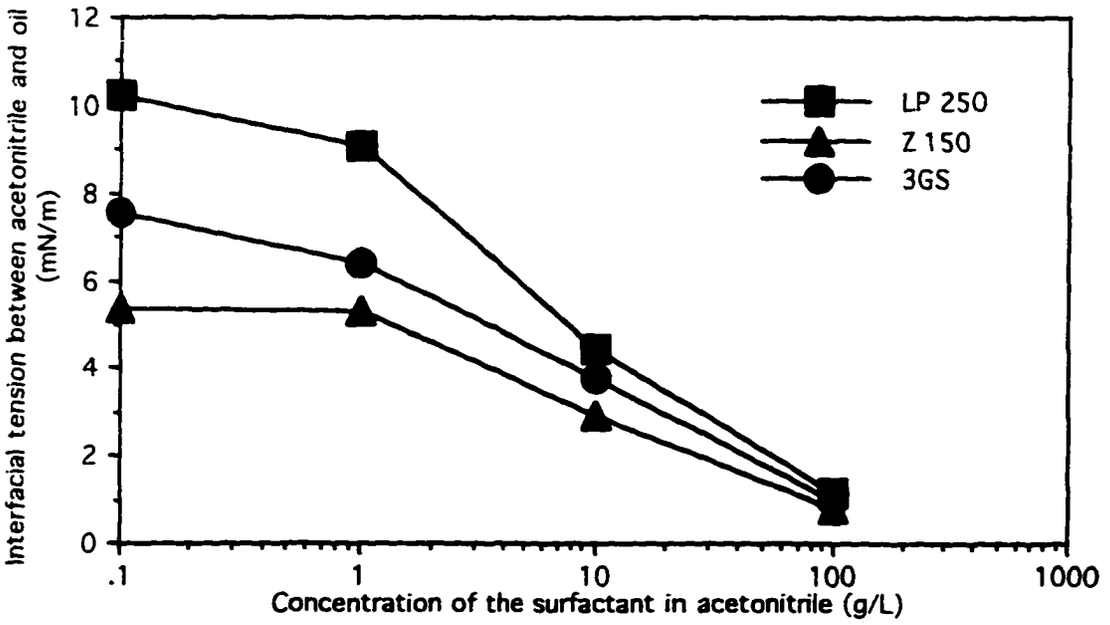

Figure 2.3.2.1 Interfacial tensions for Polychol 15 Laneth 15 surfactant.

LP 250 γ(mN/m)	Z150 γ(mN/m)	3GS γ(mN/m)	Conc. (g/L)
6.2	3.0	3.8	20
8.3	4.7	6.4	0.1
10.4	5.4	6.8	0

Table 2.3.2.2 Interfacial tensions for CROVOL A 40 surfactant.

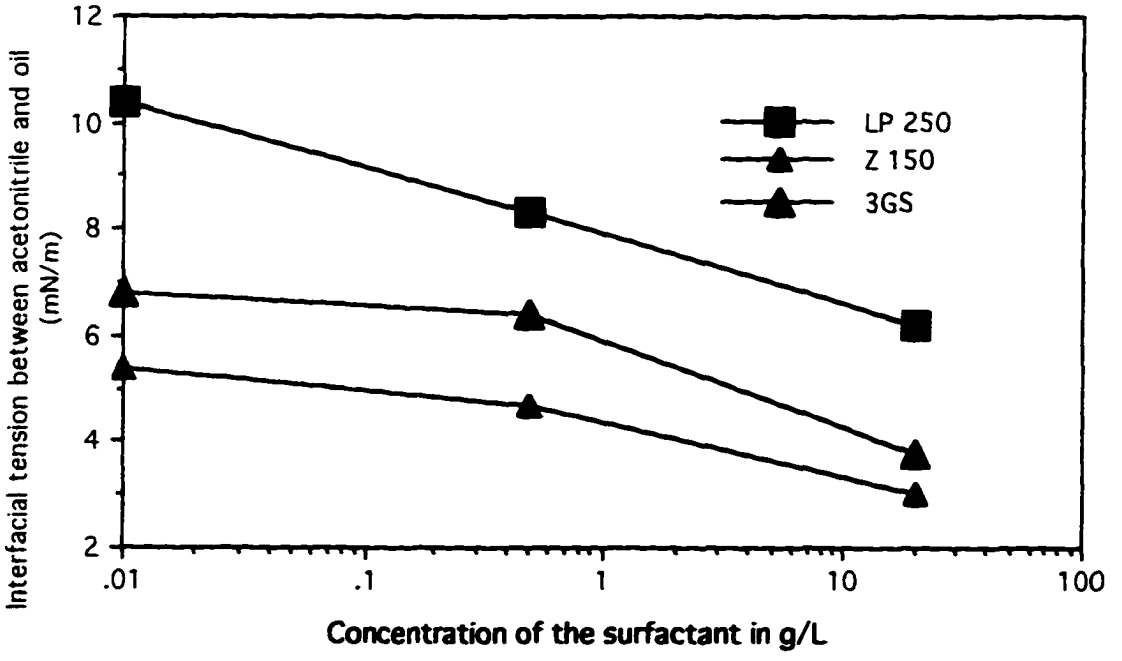

Figure 2.3.2.2 Interfacial tensions for CROVOL A 40 surfactant

LP 250 γ(mN/m)	Z150 γ(mN/m)	3GS γ(mN/m)	Conc. (g/L)
0.8	1.5	1.1	100
1.6	1.9	1.5	10
3.8	2.4	3.9	1
10.4	5.4	6.8	0

Table 2.3.2.3 Interfacial tensions for Emulphor EL 620 surfactant.

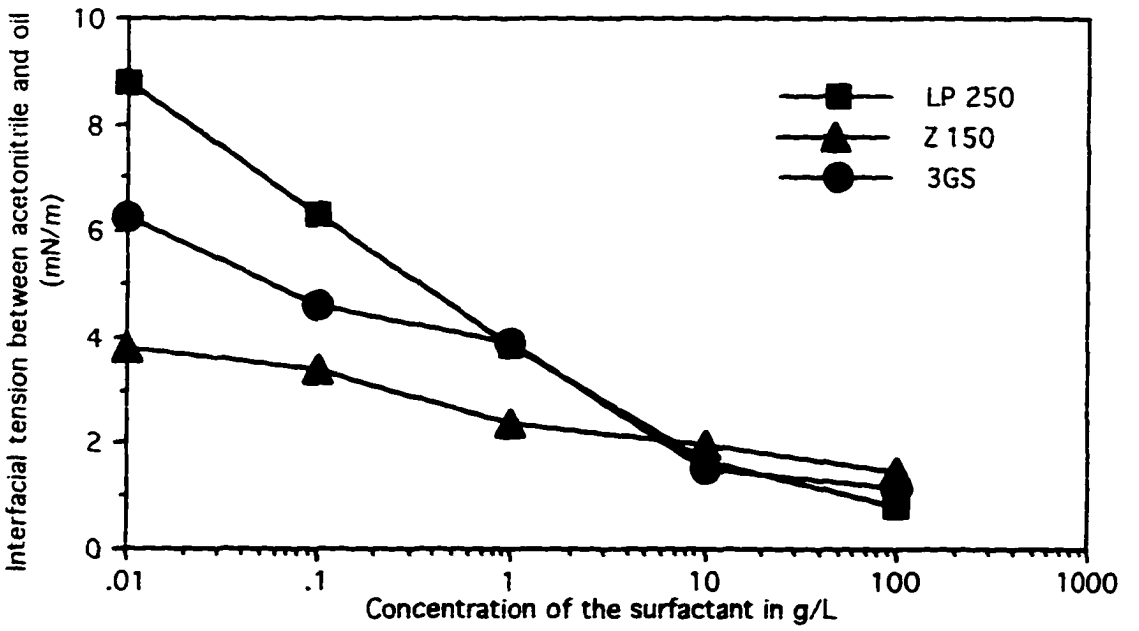

Figure 2.3.2.3 Interfacial tensions for Emulphor EL 620 surfactant.

2.4 Conclusions and Future Work

Kemester EX 1038, Kemester EX 1039 and Kenamine N-989 surfactants do not lower significantly the interfacial tension below 10 g/L concentration, and are thus not suitable for further experimentation, on the basis of the model used in the current study. Commercial surfactants that did not yield an emulsion are no good either because they are generally designed for oil/water systems and the difference in dielectric constants between water (ε=81.1) and acetonitrile (ε=37.7) is large. Emulphor EL 620, Polychol 15 Laneth 15 and Crovol A 40 seem to show promising emulsifying properties but are not effective in forming microemulsions. Therefore we had to consider other ways to solve the problem.

We found a possible alternative pathway to the desired miscibility/dispersibility enhancement. It was suggested by the cosolubilization effect of a non-surfactant compound polyoxypropylene (3) myristyl ether, PPG3M, on ethanol (ε=24.3)/mineral oils. Table 2.4 presents our initial results with this amphiphile showing that it looks promising for microemulsion formation. Thus we focused our efforts and performed a systematic microemulsion study on this new and interesting dual-end molecule.

Oil	LP 250	Z 150	Z 300	1GS	3GS	4GS
PPG3M	21 %v/v	3 %v/v	4 %v/v	14 %v/v	18 %v/v	20 %v/v

Table 2.4. **Amount of PPG3M necessary to titrate to clarity a 50/50%v/v mixture of mineral oils and absolute ethanol. (oil+ethanol=100% v/v)**

2.5 References

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Chapter 3

Non-aqueous Microemulsions from EtOH/*n*-Hexadecane Systems

3.1 Introduction

As we summarized in Chapter 1, only a few non-aqueous systems for the formation of microemulsions have been studied, with the dielectric constant in all cases being larger than 30. To further study the formation and structures of non-aqueous microemulsions of low dielectric systems and explore the cosolubilization effect of polyoxypropylene (3) myristyl ether on the mineral oil/ethanol pair we found in Chapter 2, we will conduct a systematic microemulsion study with a series of polyoxypropylene alkyl ethers as the microemulsifier. To simplify the problem, we will use *n*-hexadecane as the model for the hydrocarbon component instead of mineral oils. We use the standard titration method to obtain clear mixtures and to observe typical features associated with microemulsions (1, 2). Based on the observed features for these liquid mixtures, we propose possible states of organization, including non-aqueous microemulsions, for the mixtures. We will then perform several state-related experiments to exclude non-microemulsion states and confirm the microemulsion state and also to identify the type of the non-aqueous microemulsions prepared. Finally, we will use the Rosano method (3, 4, 5) to determine the radius of the spherical droplets of the non-aqueous microemulsions.

3.2 Experimental

Materials

The following series of polyoxypropylene alkyl ethers (PAE) were used as the microemulsifier for the study of the formation of non-aqueous microemulsions. They were kindly supplied by Croda Incorporated, Parsippany, New Jersey. They are listed below with their designation, molecular weight (MW), density at 20°C (d) and refractive index at 20°C (n).

PPG3M: Polyoxypropylene (3) myristyl ether: n-$C_{14}H_{30}O(CH_2CHCH_3O)_3H$

MW = 388 g/mol d = 0.895 kg/L n = 1.4420

PPG10C: Polyoxypropylene (10) cetyl ether: n-$C_{16}H_{34}O(CH_2CHCH_3O)_{10}H$

MW = 822 g/mol d = 0.9 kg/L n = 1.4445

PPG30C: Polyoxypropylene (30) cetyl ether: n-$C_{16}H_{34}O(CH_2CHCH_3O)_{30}H$

MW = 1982 g/mol d = 0.9 kg/L n = 1.4455

PPG50C: Polyoxypropylene (50) cetyl ether: n-$C_{16}H_{34}O(CH_2CHCH_3O)_{50}H$

MW = 3142 g/mol d = 0.9 kg/L n = 1.4460

n-Hexadecane (n-$C_{16}H_{34}$), >99% pure, Aldrich product.

Ethanol (EtOH), absolute, 200 proof, AABER product.

Titration

We used the standard titration method (1, 2) to form microemulsions. While stirring, mixtures of absolute ethanol and *n*-hexadecane were titrated to clarity using a burette filled with the microemulsifier. The ethanol composition of the mixtures and the volume ratio and the molecular ratio of the microemulsifier necessary to titrate to clarity are calculated as follows:

$$\text{Ethanol (\%v / v)} = \frac{\text{Volume of ethanol}}{\text{Volume of (ethanol + n-hexadecane)}} \times 100$$

$$\text{Surfactant (\%v / v)} = \frac{\text{Volume of surfactant}}{\text{Volume of (ethanol + n-hexadecane)}} \times 100$$

$$\text{Surfactant (\%mol / mol)} = \frac{\text{Number of moles of surfactant}}{\text{Number of moles of (ethanol + n-hexadecane)}} \times 100$$

These calculations make it easy to compare the efficiency of the microemulsifier.

Electrical Resistance Measurement

A Fluke digital multimeter (Model 77) and a platinum glass electrode was used the in measuring the electrical resistance. Figure 3.2.1 shows the experimental arrangement. Samples were contained in a 15 mL vial and continuously stirred during measurement. The electrical resistance ratios of sample to pure ethanol were plotted against the composition of the *n*-hexadecane/ethanol mixture before titration for analysis.

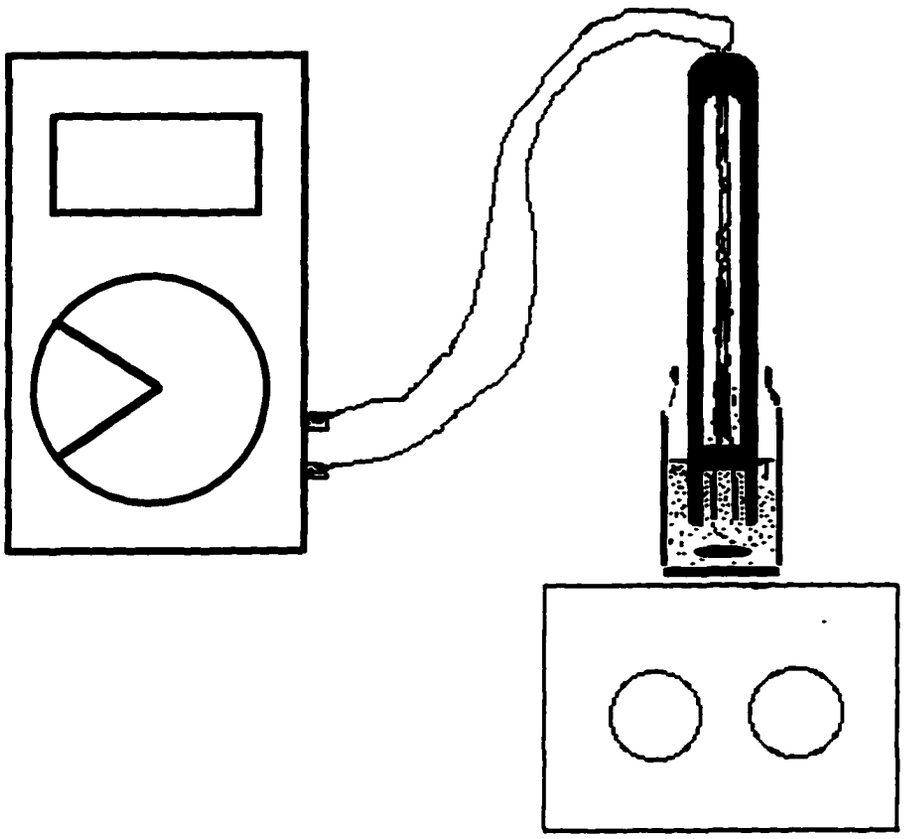


Figure 2.2.1 Electrical Resistance Measurement Set-up.

Monolayer Experiment

We used Schulman-Stenhagen and Schulman-Rideal techniques (6) to investigate the collapse pressure of monolayers of PPG3M, PPG10C, PPG30C and PPG50C. The technique was also previously described by Christodoulou and Rosano (7). The classical subphase (in which the surfactants are not soluble) used in the laboratory was a saline solution with the following composition:

- NaCl: 5.1 g/L
- Na_2HPO_4: 3.2 g/L
- NaH_2PO_4: 1.8 g/L
- EDTA: 0.6 g/L

A hexane solution of PPG3M, PPG10C, PPG30C or PPG50C was spread on the subphase. After the hexane evaporated, a monolayer of each polyoxypropylene alkyl ether was formed. The variation of the surface pressure versus the surface area per molecule of PPG3M, PPG10C, PPG30C and PPG50C at 24°C was plotted for each amphiphile.

Computer Modeling

Computer modeling of PAE amphiphiles and their interaction with ethanol and *n*-hexadecane was carried out on a Silicon Graphics workstation using Biosym software Insight II (version 2.3.0) (8) and Discover (version 2.9.5) (9). The forcefield used was *cvff*. The parameter of CUT OFF was 100 Å. Iteration of minimization calculation was 1000. The maximum derivative is less than 0.01 kcal/Å.

3.3 Results and Discussion

3.3.1 *n*-Hexadecane and Ethanol System Titrated to Clarity with Polyoxypropylene Alkyl Ethers

The minimal amount of each microemulsifier required to yield clear mixtures of *n*-hexadecane and absolute ethanol is shown in Figures 3.3.1. Observed repeatedly for long times (several months to more than three years), these liquid mixtures were transparent and stable, and the transition from milky appearance to clear was spontaneous and very well defined during titration. Liquid mixtures prepared with all four polyoxypropylene alkyl ethers showed these features.

3.3.2 Possible States of Organization in the Liquid Mixtures Prepared

Based on these features observed above, there are three possible states of organization in the liquid mixtures, as following:

1) Matching Refractive Indexes

2) Cosolubilization

3) Non-aqueous Microemulsion

In the first case, the refractive indexes of the oil phase at top and the ethanol phase at bottom simply match each other, leaving no visual difference to the observer. In the other two cases, both systems are transparent and stable because their formations is, in both cases, thermodynamically favorable, and their appearances are all macroscopically homogeneous. To differentiate these states and identify the microemulsion state, we therefore performed several standard state-related experiments.

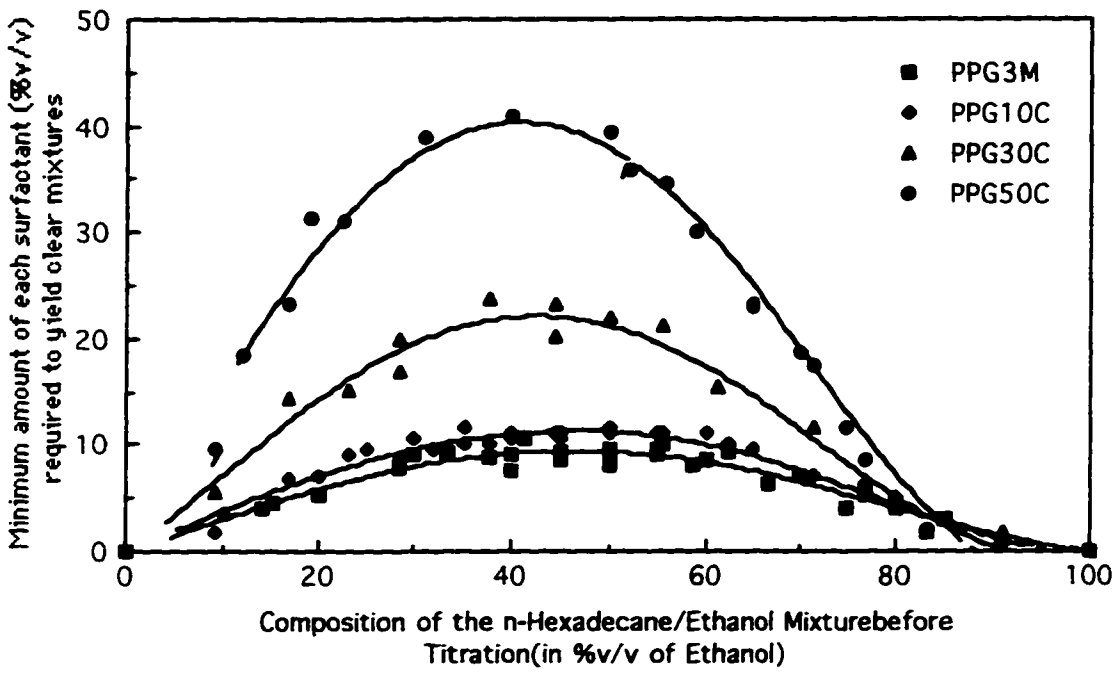


Figure 3.3.1 Minimum amount of each microemulsifier (% v/v) required to yield clear mixtures of ethanol and *n*-hexadecane versus the composition of the mixtures before titration to clarity in % v/v of ethanol.

3.3.3 Identification of the Microemulsion State and Type

An initial finding was that there is, in fact, no matching of the refractive indices. Mixtures of ethanol and the microemulsifier were prepared at different ratios and the refractive indices were measured at 20°C using an Abbe refractometer. Mixtures of *n*-hexadecane and the microemulsifier were studied in the same manner. Figure 3.3.3.1 shows the refractive index of each of the two mixtures versus the composition (%v/v) in PPG3M.

As shown in the diagram, the refractive indices of the mixtures *n*-hexadecane /PPG3M and ethanol/PPG3M never have the same value (and this result is observed with all four polyoxypropylene alkyl ethers). In other words, matching of the refractive indices is impossible, ruling out our first possible explanation.

In order to propose a state of organization between a cosolubilization and non-aqueous microemulsions, we studied the variations of the electrical resistance of the clear mixture. The relative electrical resistances of the different clear mixtures are shown in Figure 3.3.3.2.

The electrical resistance of the clear systems indicates that below about 40%v/v of ethanol the mixtures titrated with PPG3M have an electrical resistance similar to that of *n*-hexadecane. Above this amount of ethanol the electrical resistance is identical to that of pure ethanol.

From the diagram, we also see this happened with all polyoxypropylene alkyl ether systems, indicating this behavior is determined by the structure of the polyoxypropylene alkyl ethers.

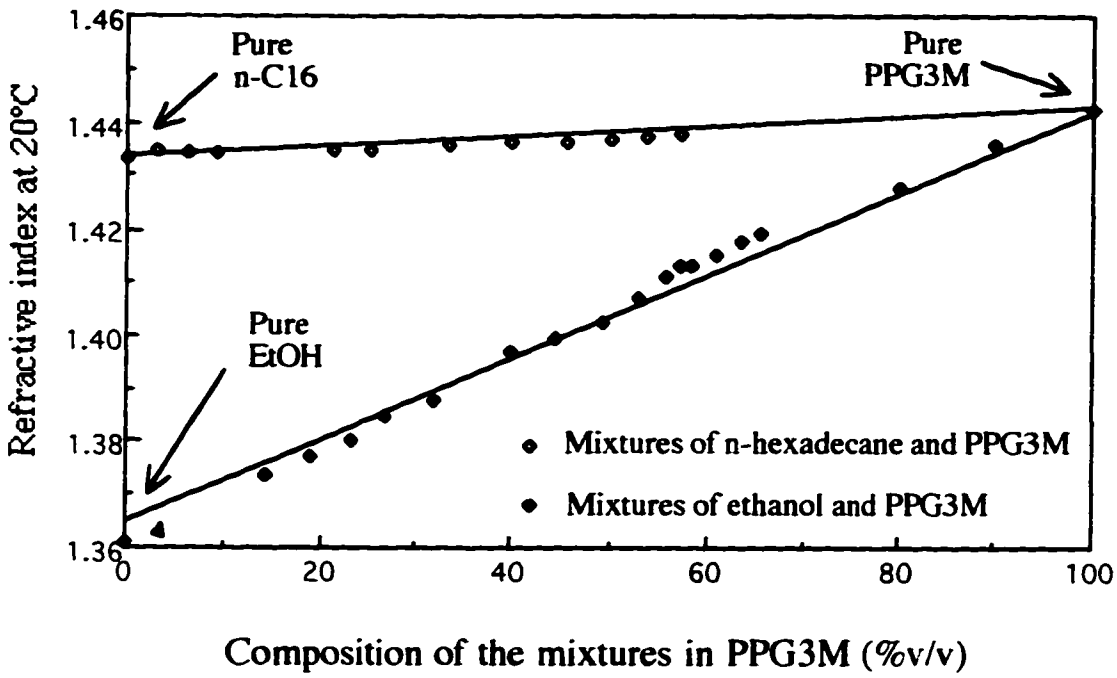


Figure 3.3.3.1 Refractive index of each of the two mixtures versus the composition (%v/v) in PPG3M.

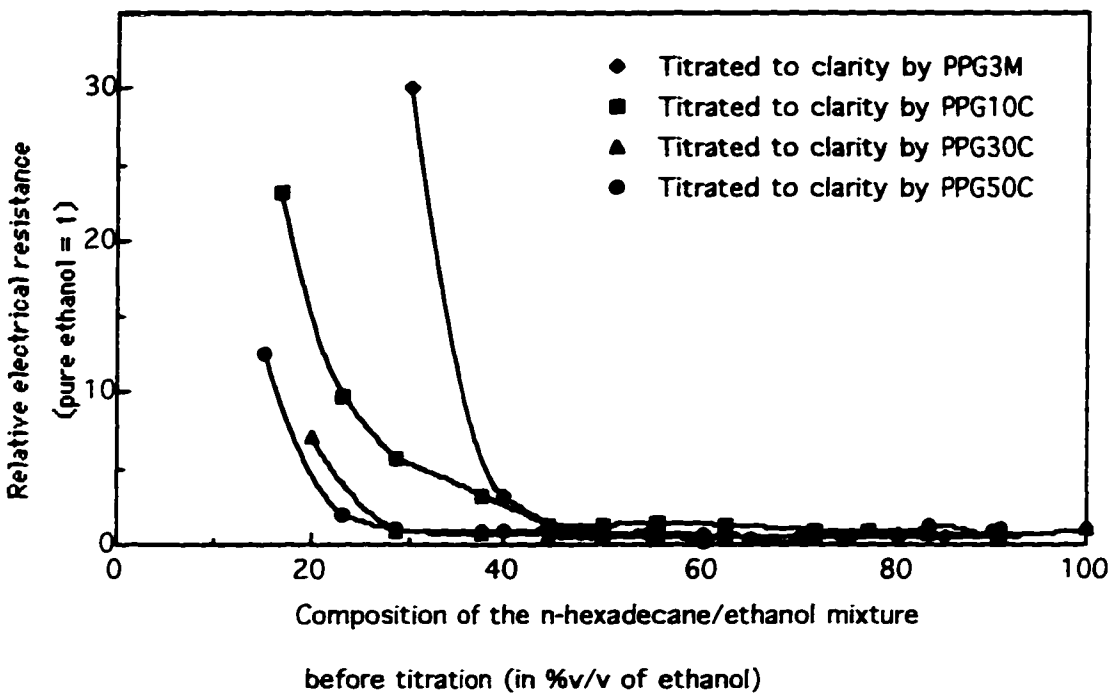


Figure 3.3.3.2 Electrical Resistance Measurement.

With cosolubilization, the electrical resistance would not present this kind of break. Thus, the optical clarity of all the systems led us to believe, for the mixtures titrated to clarity with PPG3M, structures consist of non-aqueous microemulsions of ethanol-in-*n*-hexadecane below 40% v/v of absolute ethanol and of microemulsions of *n*-hexadecane-in-ethanol above 40% v/v of ethanol.

To further confirm our interpretation of the structure as a non-aqueous microemulsion, and to determine the type of dispersion, we added two drops of each solvent to the clear mixtures of ethanol and *n*-hexadecane titrated to clarity with PPG3M, PPG10C, PPG30C, or PPG50C in a test tube, which was subsequently shaken and observed visually. The results are shown in Figure 3.3.3.3. In the diagram, white regions indicate that the system remains clear after addition of a single drop of solvent to the ethanol/hexadecane/microemulsifier mixture; dark regions indicate that the system becomes cloudy after addition of a single drop of solvent to the mixture. Such properties are consistent only with non-aqueous microemulsions because the amount of the microemulsifier used in titration was minimum (see Figure 3.3.1).

We also notice that microemulsifiers containing longer polypropylene glycol chains in their molecule preferentially form *n*-hexadecane-in-ethanol non-aqueous micro-emulsions. This is because the longer polypropylene glycol chain tends to form a bigger polar head and can interact with ethanol more intensively. This has been seen from the results of our monolayer experiment (next section, see Figures 3.3.4.1 & 2), H^1-NMR study (Chapter 5), and computer modeling (next section, see Figure 3.3.4.3).

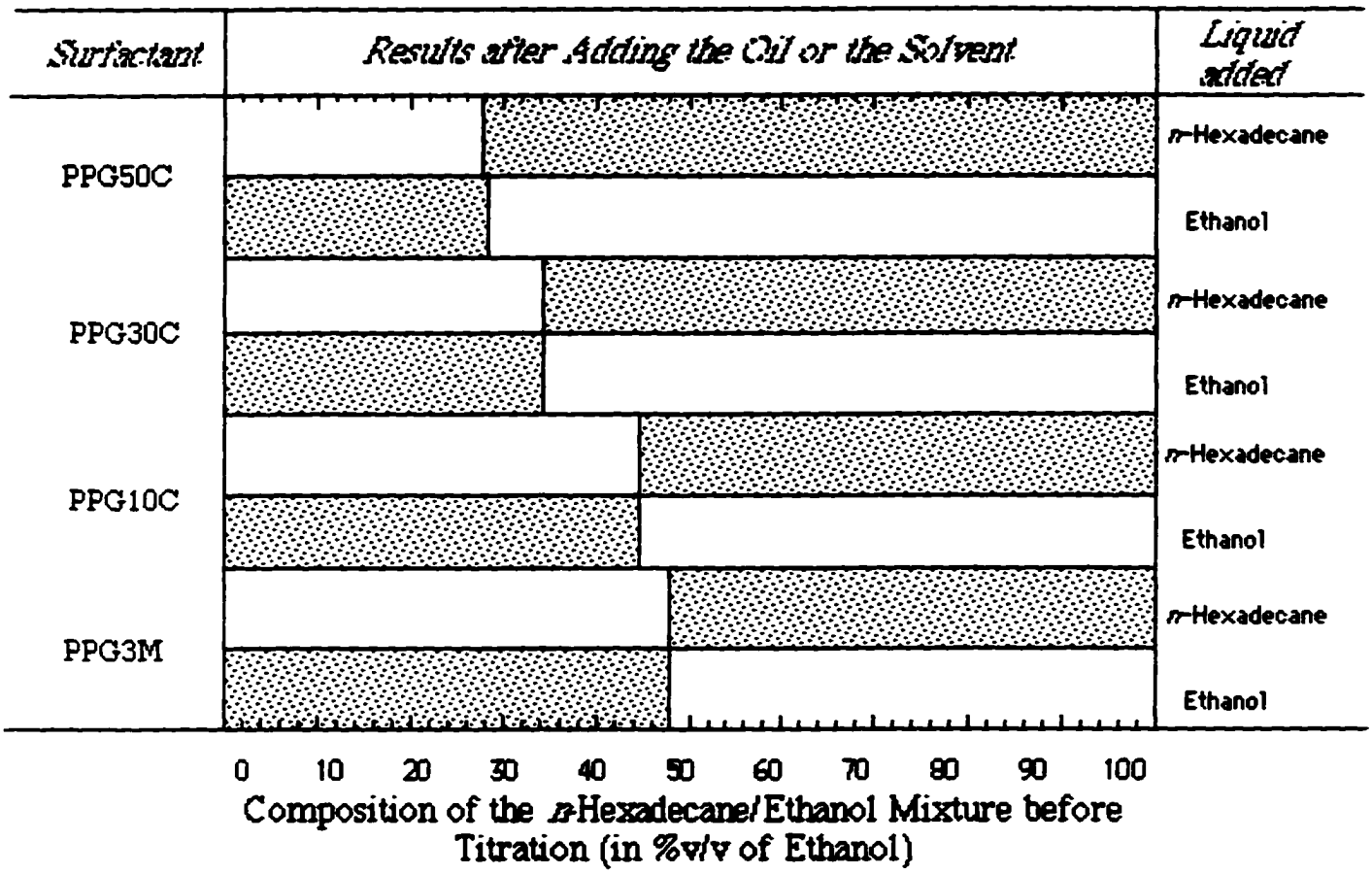


Figure 3.3.3.4 Dilution/Addition Tests.

3.3.4 Calculation of the Diameter of the Spherical Droplets

Rosano (3, 4) suggested a way to determine the radius of spherical droplets when the minimum amount of surfactant needed for a particular system is known. If a given volume (V) of a phase is dispersed into spherical droplets of radius r (Å), the total volume of the dispersed phase can be expressed as:

$$V = a\frac{4}{3}\pi r^3 \qquad (1)$$

where a is the total number of droplets formed by the dispersed phase. The total surface area A of the droplets is:

$$A = a\,4\pi r^2 \qquad (2)$$

$$A = \sigma n \qquad (3)$$

where σ is the interfacial area of the surfactant molecule and n the number of molecules of surfactant. Combining Eqs. 1, 2, and 3, and solving for r, we find:

$$r = \frac{3V}{n\sigma} \qquad (4)$$

The value of σ was obtained from monolayer measurements. We used Schulman-Stenhagen and Schulman-Rideal techniques to obtain the collapse pressure of monolayer. Figure 3.3.4.1 and Figure 3.3.4.2 show the variation of the surface pressure versus the surface area per molecule of PPG3M, PPG10C, PPG30C and PPG50C at 24°C.

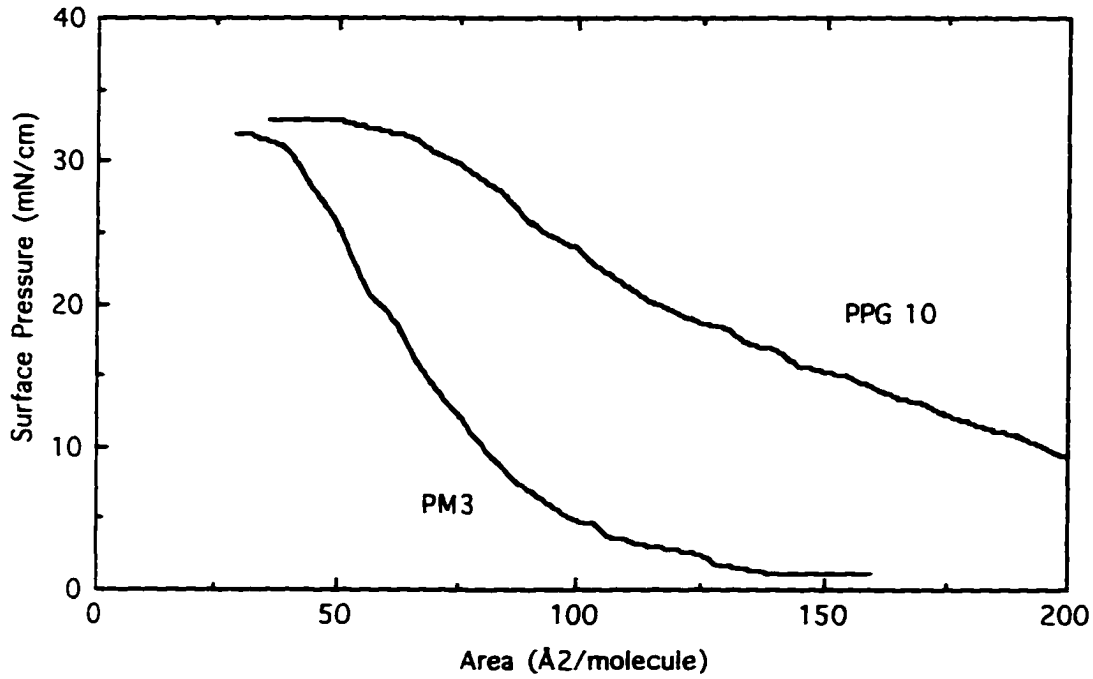


Figure 3 3.4.1 Variation of the surface pressure versus the surface area per molecules of PPG3M and PPG10C.

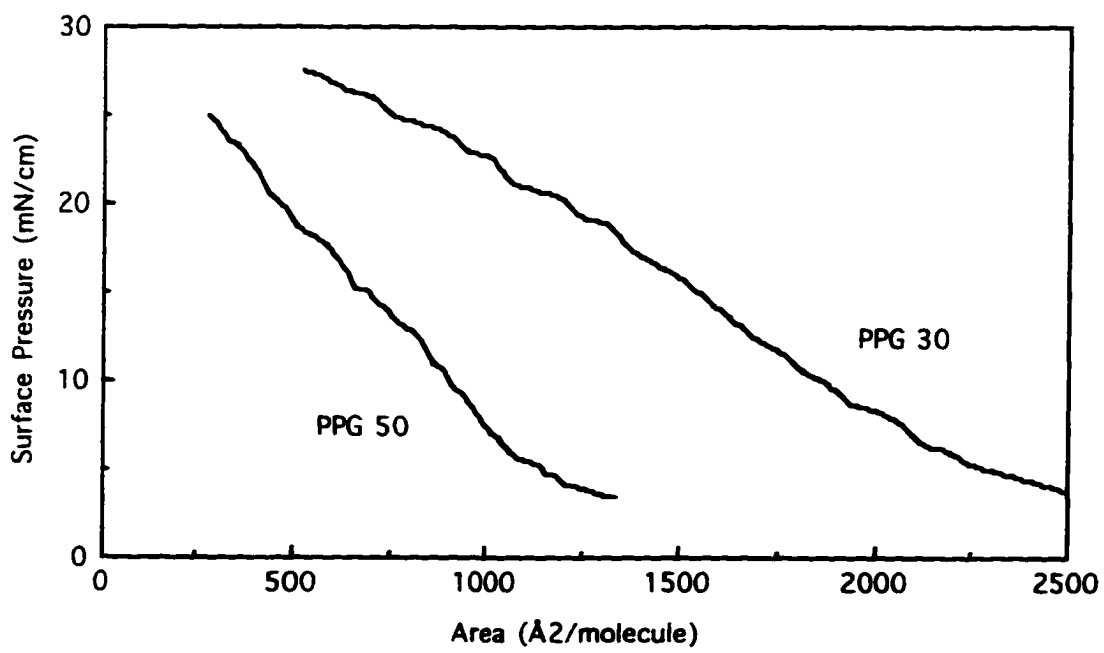
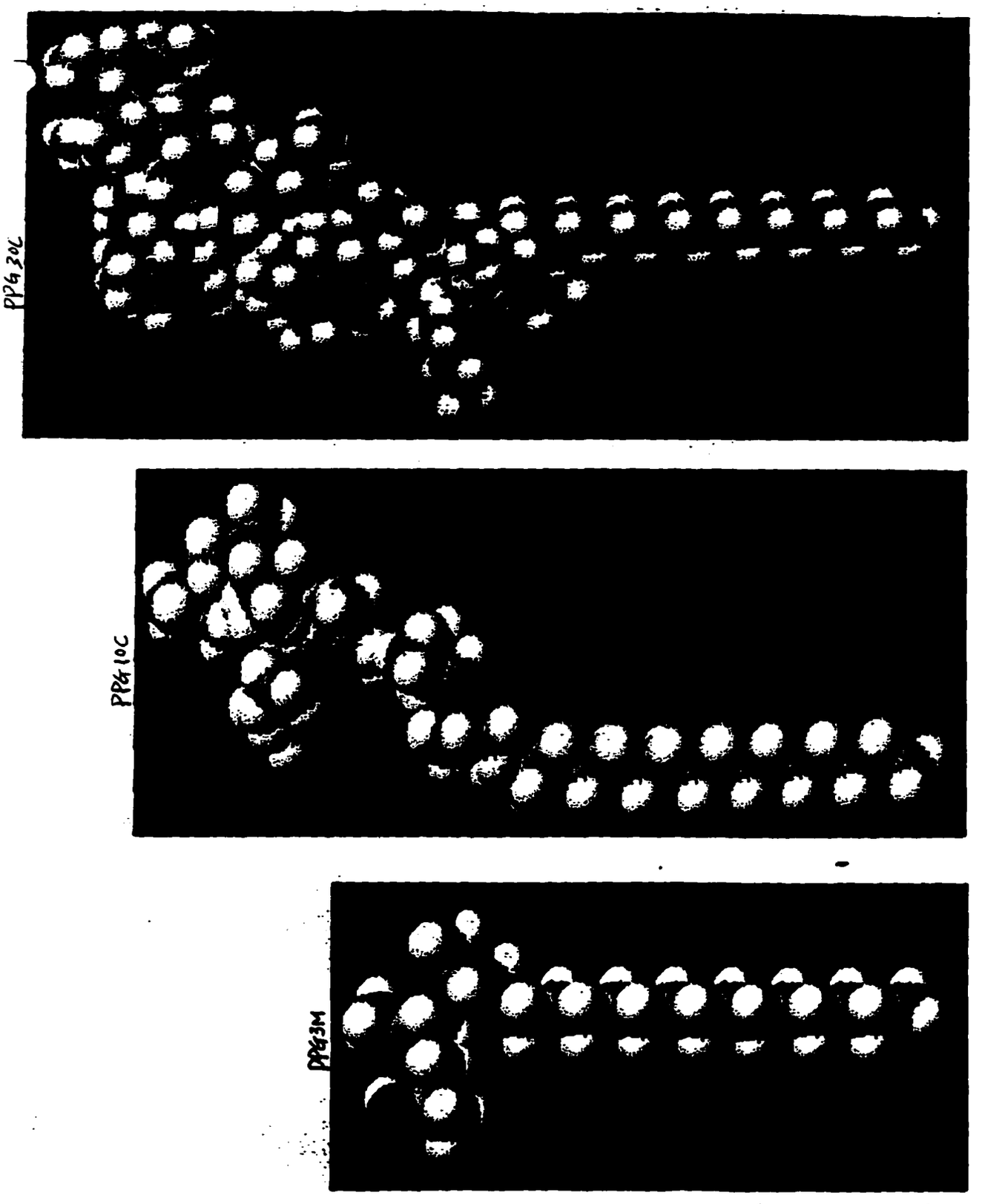


Figure 3.3.4.2 Variation of the surface pressure versus the surface area per molecules of PPG30C and PPG50C.

Figure 3.3.4.3 Computer Modeling of PPG3M, PPG10C and PPG30C.

(See Section 3.2 for modeling parameters)



The isotherms of compression show an increase in surface area from PPG3M to PPG10C and no collapse for PPG30C or PPG50C. This is due to the increase in length of the PPG polar chain in these molecules which makes the polar head larger in size, and an increasing inability for these molecules to assume a vertical orientation. This increase in the size of the polar head (10) can be clearly seen from our computer modeling results using Biosym software on a Silicon Graphic workstation, as shown in Figure 3.3.4.3.

Assuming that the interfacial area, σ, of the PPG3M is equal to 40Å^2/molecule (the value at the collapse pressure, as shown in Figure 3.3.4.1), we calculated the diameter of the dispersed droplets from equation (4). Figure 3.3.4.4 plots this diameter versus the amount of ethanol (v/v %).

Above 40-50 %v/v of ethanol, the calculated diameter of the droplets of *n*-hexadecane-in-ethanol is stable at about 500 Å; this is compatible with the transparency as observed.

Below this amount of ethanol, the calculated diameter increases and becomes larger than 1000 Å, according to equation (4), if we assume this type of droplet still exists. But, based on this hypothesis, the system could not be clear because for microemulsions, the upper limit of the diameter is 1000 Å (1/4 the wavelength of visible light). This is incompatible with the transparency as observed and suggests to us the system is composed of ethanol-in-*n*-hexadecane type droplets, with a smaller diameter, below the microemulsion diameter limit.

Thus we carried out the diameter calculations for this type of droplets. The results show that below 40-50 %v/v of ethanol, the calculated diameter is stable at about 350 Å and this is compatible with the transparency as observed. Above this amount of ethanol,

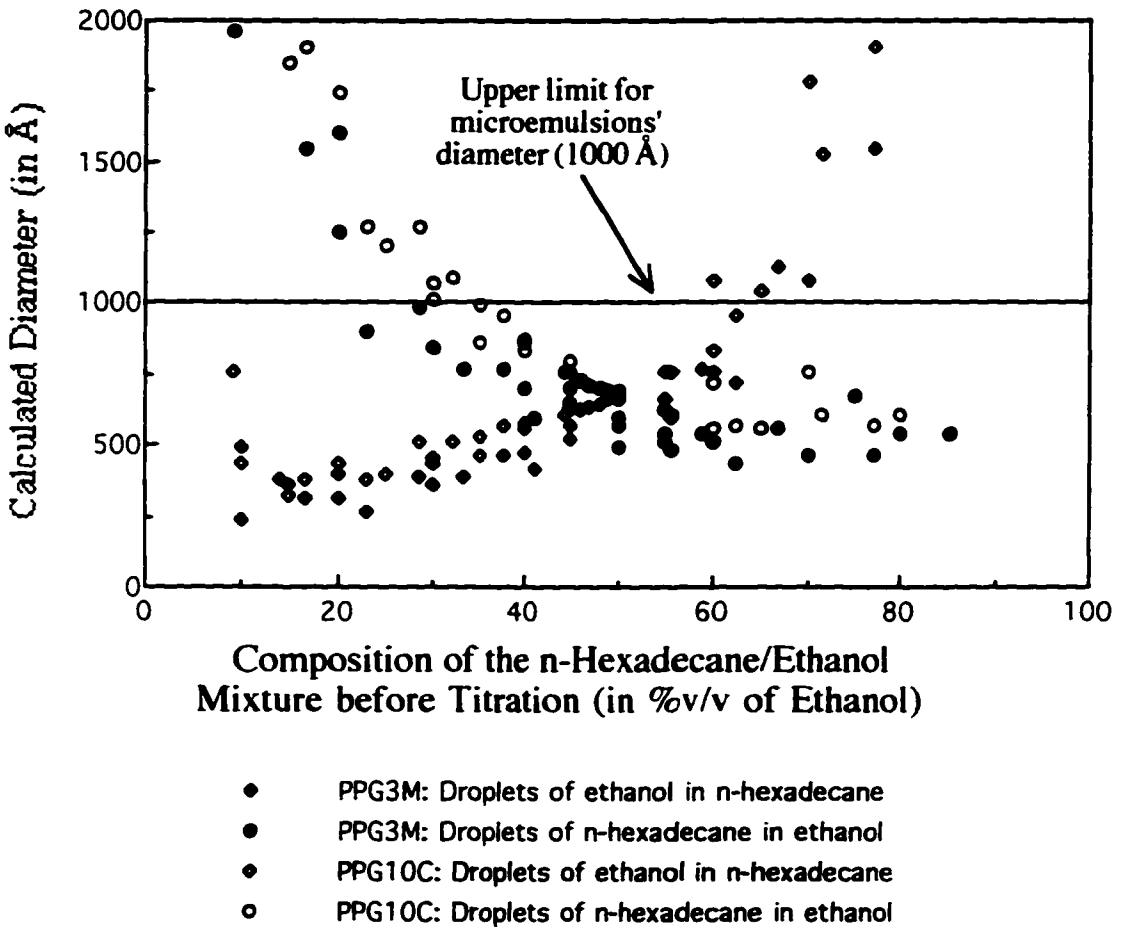


Figure 3.3.4.4 Calculated diameters of microemulsion droplets.

the calculated diameter increases and becomes larger than 1000 Å; this is incompatible with the transparency as observed, and tells us that this type of ethanol-in-*n*-hexadecane microemulsion does not exist when the ethanol amount is larger than 60 % v/v.

For both calculated radius values, the graph shows a dramatic break at a constant ratio (40-50% v/v), which reinforces the hypothesis of the formation of non-aqueous microemulsions.

Also for mixtures titrated to clarity with PPG10C (interfacial area of 60Å^2/molecule), similar conclusions are reached. The dispersed droplets have about the same diameter (Figure 3.3.4.4).

The calculations carried out here only provide us a qualitative or semi-quantitative identification of the non-aqueous microemulsions, because the method was based on the assumption of a compact interface for classic aqueous microemulsions. The results we obtained here suggest a loose, fuzzy interface which consists of the amphiphile molecules with much larger polar head, penetrated by ethanol and *n*-hexadecane. This will be seen again in the following studies.

3.4 Summary

In this chapter, we have performed a systematic microemulsion study on the ethanol/*n*-hexadecane model pair. We have studied the cosolubilization effect we found in Chapter 2 using a series of polyoxypropylene alkyl ethers and have successfully prepared microemulsions for our low dielectric model system by the standard titration method. We have examined all possible states of organization for the liquid mixtures we prepared and have identified the microemulsion states and confirmed them with state/type-related experiments typically used for aqueous microemulsions. We also studied the amphiphiles' behavior at the water/air interfaces with the monolayer experiment and computer modeling and have calculated the droplet size for both types of microemulsions, when the head groups are small enough to permit an estimate of molecular area from collapse pressure.

3.5 References

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Chapter 4

Fluorescence Probe Study of the Formation of Ethanol/*n*-Hexadecane Non-aqueous Microemulsions

4.1 Introduction

In the previous chapters, we have reviewed and analyzed the aggregation and microemulsion behavior of certain amphiphiles in non-aqueous media; we have studied their roles in lowering the oil/solvent interfacial tension, their ability to form emulsions with the oil/solvent pair, and their ability to cosolubilize the oil/solvent pair in low dielectric systems; we have successfully formed and confirmed non-aqueous microemulsions for low dielectric systems using the ethanol/*n*-hexadecane model pair with amphiphiles in the polyoxypropylene alkyl ether series. Because little is known about amphiphile behavior in non-aqueous media, as we discussed before, and also because the polyoxypropylene alkyl ethers are a class of amphiphile not studied before, we want to conduct research into the nature of their aggregation behavior in low dielectric media (polar or non-polar) first, and then on their interaction with the ethanol/*n*-hexadecane pair, in order to understand the microemulsion formation process and mechanism in low dielectric and non-aqueous systems.

We will use the fluorescence probe method (1) as the tool for the study because of its effectiveness and sensitivity with aggregation systems compared with other aggregate-related techniques, such as light scattering. We will use pathways in the triangular phase diagram to study the formation process systematically, instead of the typical point approach for microemulsion study found in the literature (2, 3). Because there has been no

fluorescence probe study of non-aqueous systems, as we reviewed before, the study we will perform should also offer us some hints for the study of other non-aqueous systems.

4.2 Experimental

Materials

Pyrene was obtained from Aldrich Chemical Co. and was purified by recrystallization in ethanol four times. Its structure and typical fluorescence spectra in polar and non-polar media are shown in Figure 4.2.1. The feature of the spectrum we will use as the microstructural probe is the change of the fluorescence peak ratio III/I in response to the polarity of the microenvironmemt (4, 5). The spectrum, showing the peaks in polar and non-polar solvents, is shown in Figure 4.2.1. The concentrations of pyrene in the samples were kept less than $10^{-5}M$ to prevent excimer formation, as determined from the spectra.

Pyrene-1-carboxaldehyde was obtained from Aldrich Chemical Co. and was purified by recrystallization in ethanol four times. Its structure and variation of fluorescence maximum in various media are shown in Figure 4.2.2. The feature of its spectrum we will use as the microstructural probe is the change of the fluorescence maximum in response to the polarity of the microenvironment (2, 6) (see figure 4.2.2). A concentration of $2 \times 10^{-5}M$ was used.

Static Fluorescence Measurements

Fluorescence measurements were taken on a Spex Fluorescence Spectrometer. The pathways for the study of polyoxypropylene alkyl ether aggregation in ethanol (path a) and in *n*-hexadecane (path c) and for the study of the formation of *n*-hexadecane-ethanol microemulsion (path b) and of ethanol-*n*-hexadecane microemulsion (path d) are shown in Figure 4.2.3a and Figure 4.2.3b.

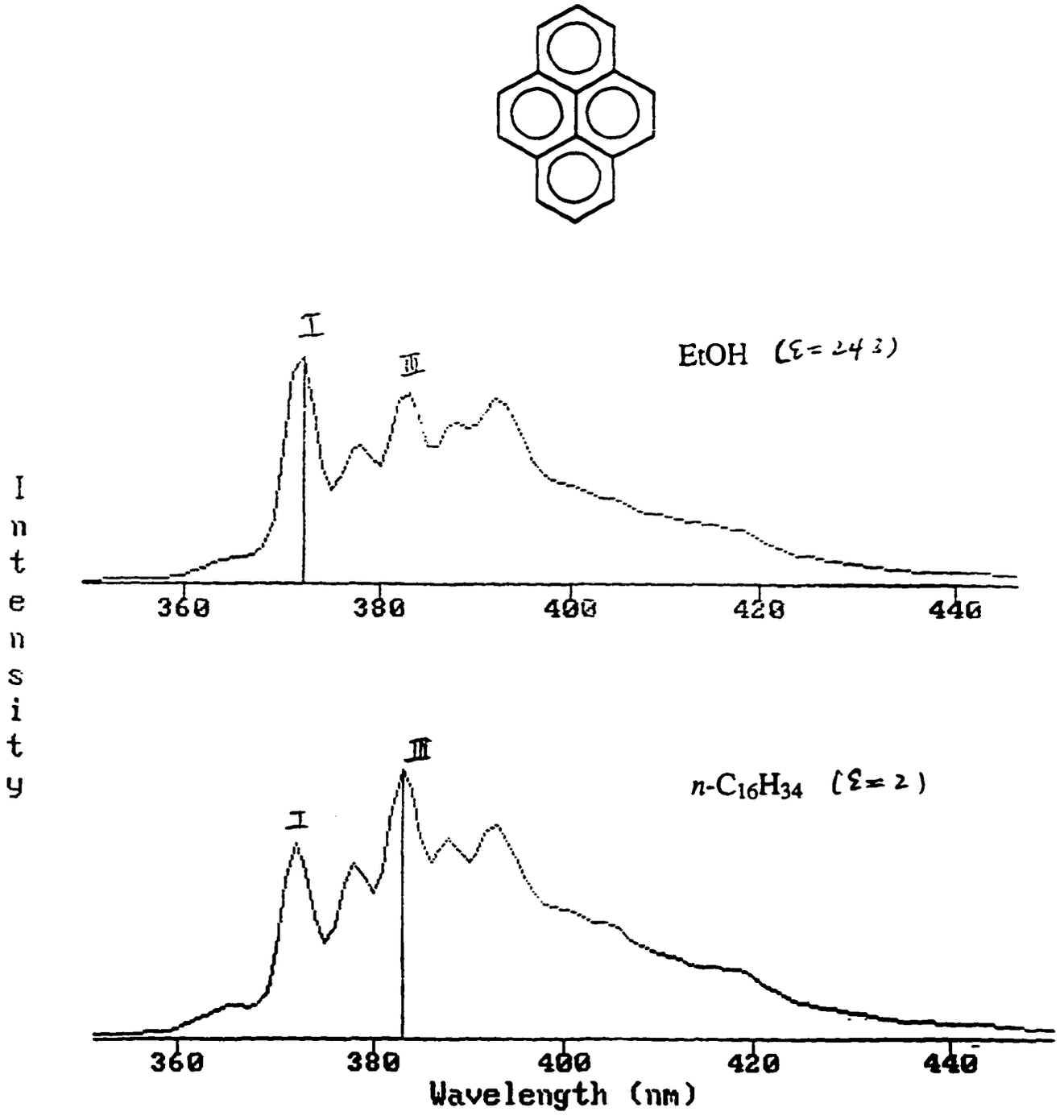
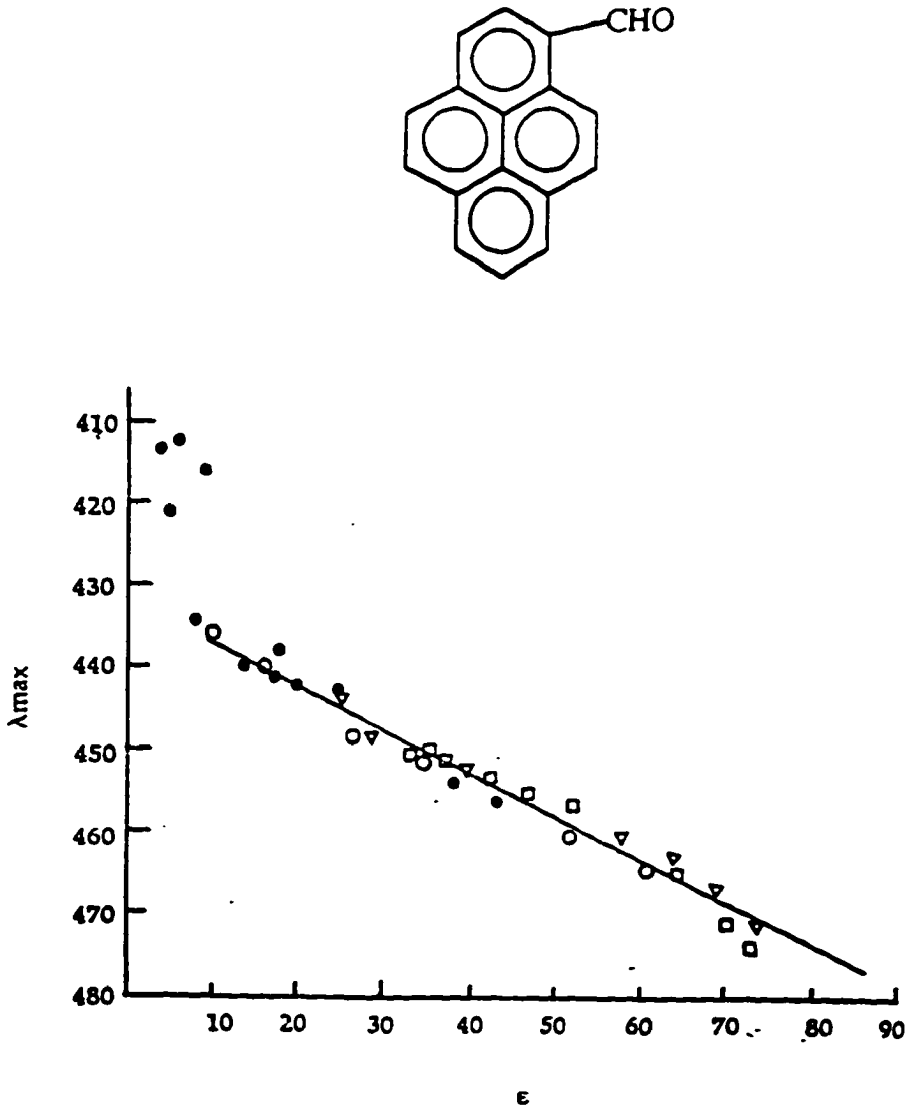


Figure 4.2.1 Pyrene Structure and Fluorescence Spectra in Polar (up) and Non-polar (bottom) Solvent.



Key: □, methanol–water mixtures; ∇, ethanol–water mixtures; ●, dioxane–water mixtures; and ○, pure solvents. Key to ε(fluorescence maximum): chloroform, 4.8 (421); chlorobenzene, 5.6 (412); dichlorobenzene, 8.9 (416); 1-hexanol, 13.5 (440); 2-propanol, 18 (438); 1-butanol, 17.5 (441); 1-propanol, 20.3 (442); ethylene glycol, 38 (456); and glycerol 43 (456) (6).

Figure 4.2.2 Variation of λ_{max}^{fluor} For Pyrene-1-Carboxaldehyde With Solvent dielectric Constant ε (reproduced from reference 6).

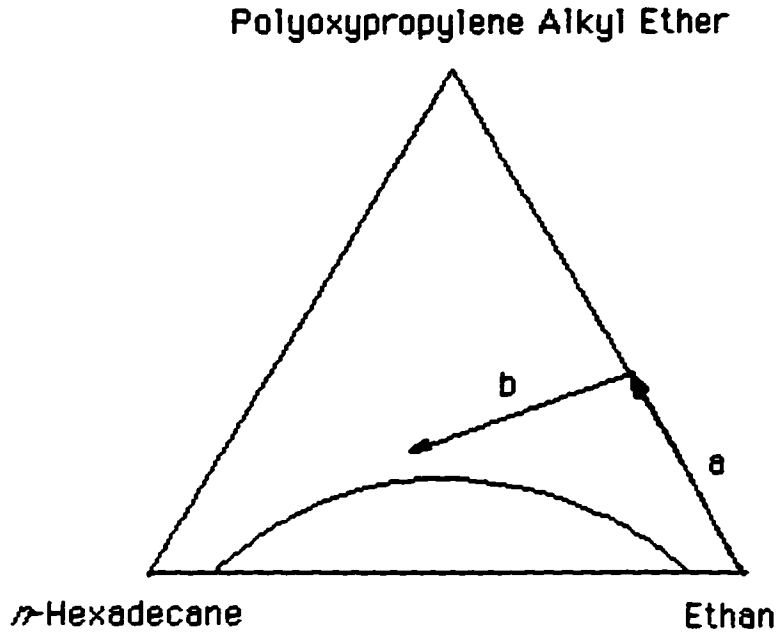


Figure 4.2.1a Pathway for Study of the Formation of n-Hexadecane-in-Ethanol Type Non-aqueous Microemulsions

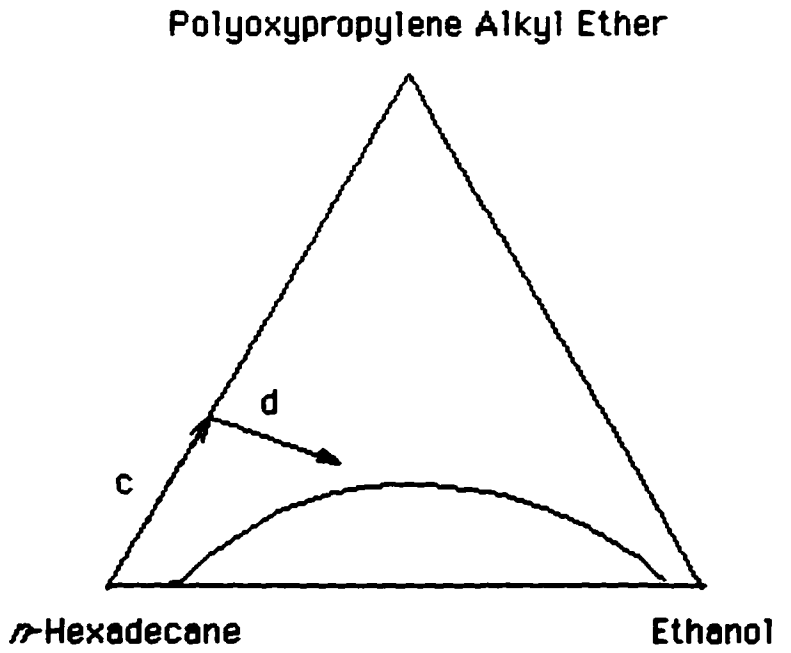


Figure 4.2.1b Pathway for Study of the Formation of Ethanol-in-n-Hexadecane Type Non-aqueous Microemulsions

Fluorescence Lifetime Measurements

Fluorescence lifetime measurements of pyrene in *n*-hexadecane-in-ethanol microemulsions were taken on the same Spex Fluorescence Spectrometer. Samples were first bubbled with nitrogen flow for at least half hour, then were sealed under nitrogen atmosphere, and frozen in liquid nitrogen. Next they were allowed to slowly thaw to room temperature and the lifetime measurements of the sample were taken. This process was repeated for several cycles until the values of the lifetime stayed stable (variation < 10%). The data was taken with the DM3000 software (version 3.2) (7) and lifetime analysis was done with the software Global Unlimited (version 3) (8). The pyrene concentration in the samples was about $10^{-7}M$.

4.3 Results and Discussion

4.3.1 Polyoxypropylene alkyl ether aggregation behavior in ethanol

To understand the formation of ethanol/*n*-hexadecane non-aqueous microemulsions, we started with the amphiphile-solvent two component system to study the amphiphile micellation in the solvent using pyrene as the microstructural probe. Since the earlier studies by Nakajima (4) and Thomas *et al* (5, 6), pyrene has been widely used for probing the formation of hydrocarbon microenvironment in various aggregate systems because of its hydrophobicity. Figure 4.3.1.1 shows fluorescence peak III/I ratio of pyrene as a function of SDS concentration in water at room temperature. As the diagram shows, the III/I ratio goes through a sharp increase from about 0.65 to 0.97-1.0 as the concentration increases, indicating a hydrocarbon core formed during micellation. The results obtained here are corresponding to those in the literature (9, 10).

Figure 4.3.1.2 shows fluorescence peak III/I ratio of pyrene as a function of PPG3M concentration in ethanol at room temperature. Obviously different from the SDS system above, the pyrene III/I ratio almost did not increase noticeably and there was almost no change even as the concentration of PPG3M reached high values (>10 % v/v), indicating the polarity of environment for pyrene molecule did not change and no hydrocarbon microenvironment formed. Polyoxypropylene alkyl ethers (PAE) are a new series of amphiphiles, so data on their properties is not available. However, this behavior is understandable because the interaction between the polar head and ethanol in our system is weaker than that between the polar head of the surfactant in regular surfactant-water micellar systems (11).

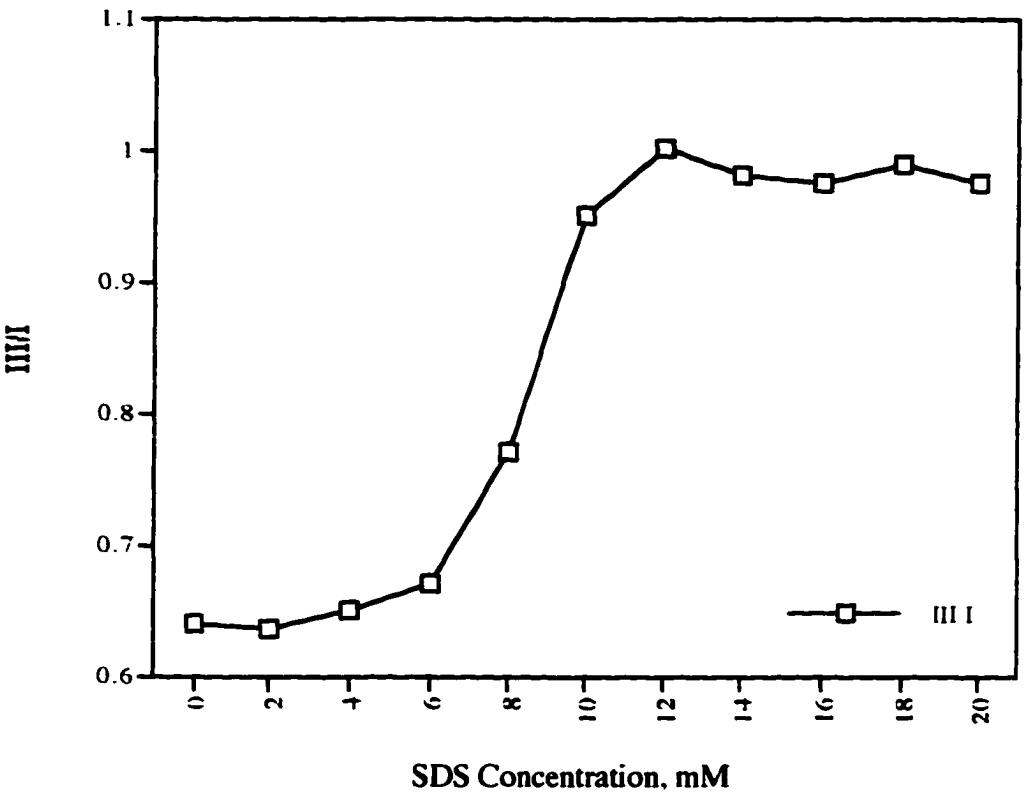


Figure 4.3.1.1 Fluorescence Peak III/I Ratio of Pyrene ($1x10^{-6}M$) as Function of SDS Concentration in water at Room Temperature.

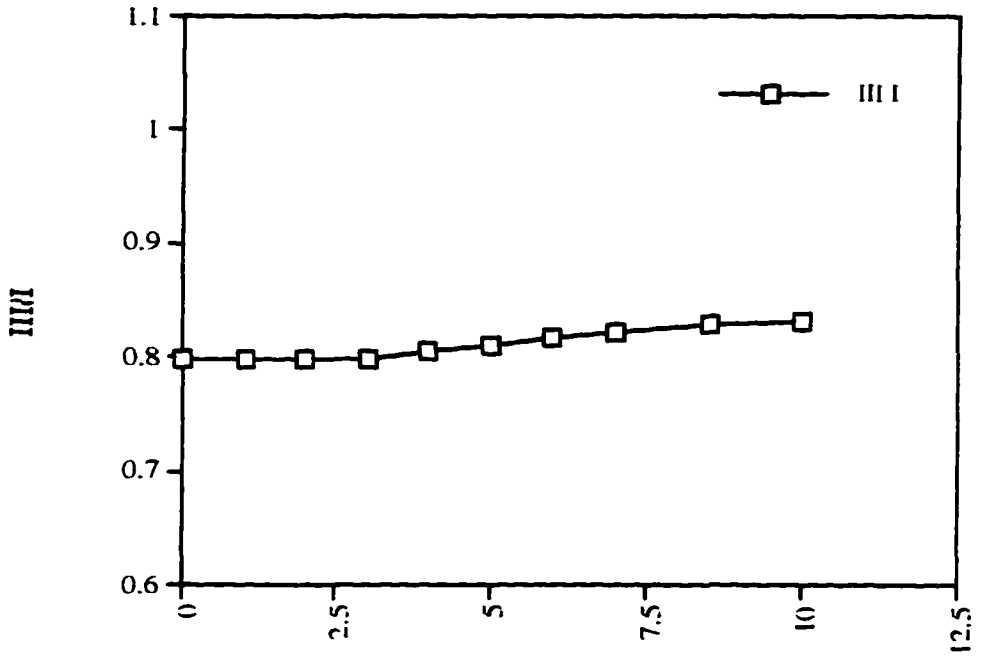


Figure 4.3.1.2 Fluorescence Peak III/I Ratio of Pyrene ($1x10^{-5}M$) as Function of PPG3M Concentration in Ethanol at Room Temperature.

To further observe and confirm this discovery of the absence of aggregation of PAE amphiphiles in ethanol, we studied the pyrene III/I fluorescence peak change for the PPG10C, PPG30C and PPG50C-ethanol systems and the results are shown in Figure 4.3.1.3, Figure 4.3.1.4 and Figure 4.3.1.5, respectively. These results again show no sharp increase in the III/I ratio and no aggregation formation although the size of the polar part is increasing in the series. The systematic observation with the series of polyoxypropylene alkyl ethers in ethanol confirms that amphiphiles like polyoxypropylene alkyl ethers do not behave in low dielectric media as surfactants do in water and the concept of micellization does not hold for low dielectric systems here.

To further enhance this understanding of amphiphile behavior in low dielectric media, we used another fluorescence probe molecule, pyrene-1-carboxaldehyde, to study the aggregation of PAEs in ethanol. Typical results with the PPG3M/ethanol system are shown in Figure 4.3.1.6. Since the earlier work of Thomas et al (2), pyrene-1-carboxaldehyde has been used for monitoring the amphiphile interface formation because of its amphiphilic structural feature and the sensitive change of its fluorescence maximum to the dielectric constant of the medium (12). The results of Figure 4.3.1.6 show no fluorescence maximum shift, indicating no change in local polarity and no formation of any amphiphile interfacial layer, different from the situation in aqueous systems (2). This confirms what we found from the above study using pyrene as the microstructural probe.

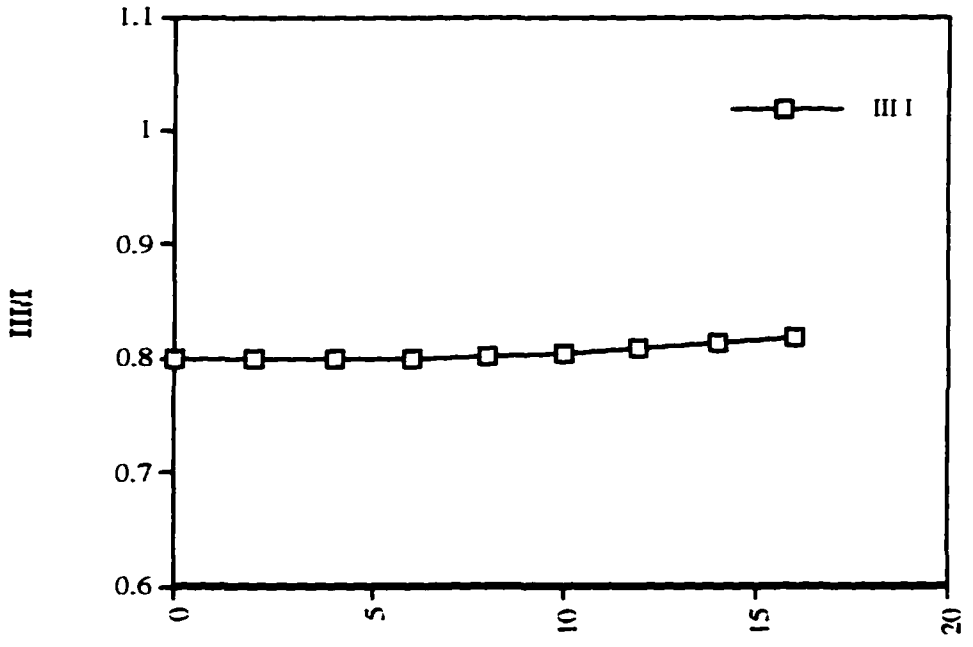


Figure 4.3.1.3 Fluorescence Peak III/I Ratio of Pyrene ($1x10^{-5}M$) as Function of PPG10C Concentration in Ethanol at Room Temperature.

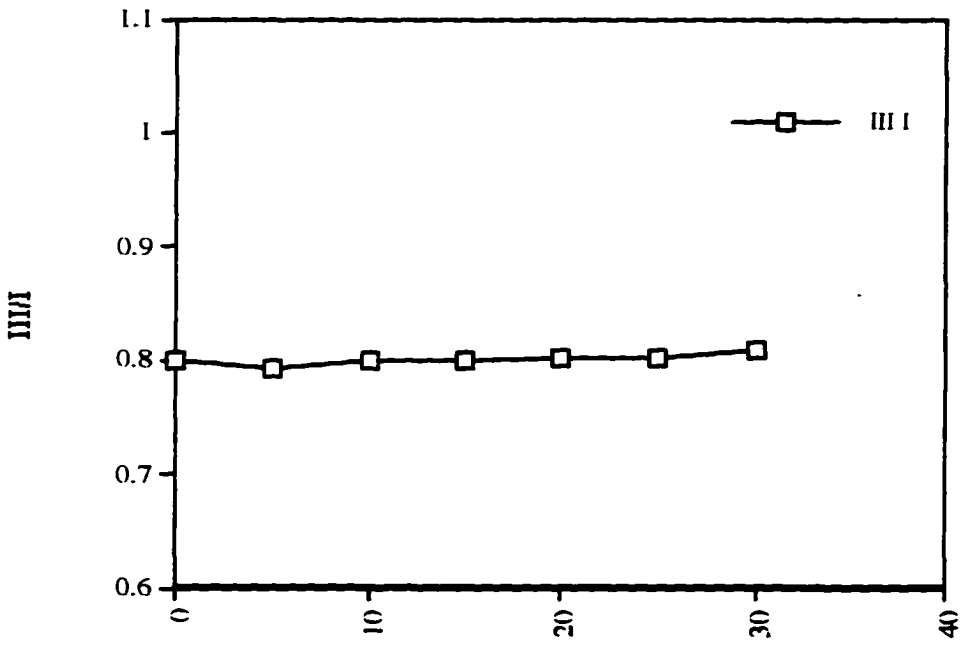


Figure 4.3.1.4 Fluorescence Peak III/I Ratio of Pyrene ($1x10^{-5}M$) as Function of PPG30C Concentration in Ethanol at Room Temperature.

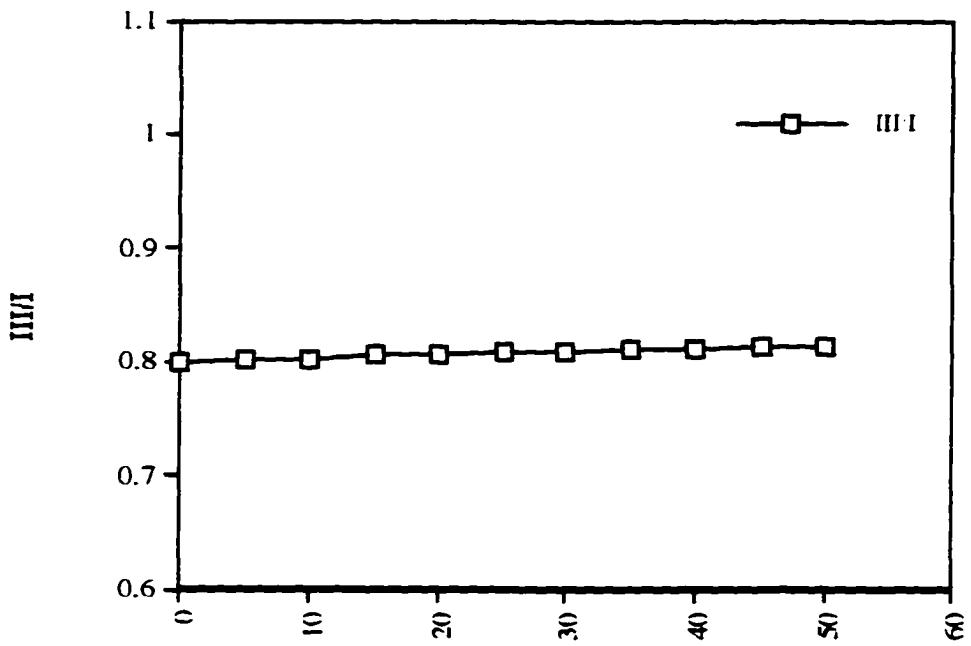


Figure 4.3.1.5 Fluorescence Peak III/I Ratio of Pyrene ($1x10^{-5}M$) as Function of PPG50C Concentration in Ethanol at Room Temperature.

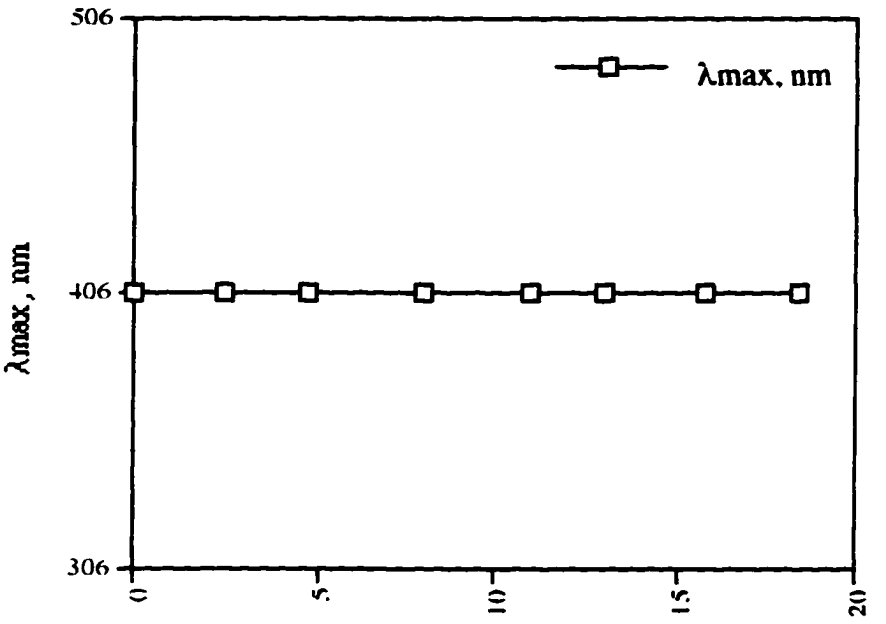


Figure 4.3.1.6 Fluorescence λmax of Pyrene-1-Carboxaldehyde ($2x10^{-5}M$) in Ethanol/PPG3M Solution as Function of PPG3M Concentration.

4.3.2 Effect of *n*-hexadecane addition on the aggregation behavior in PAE/Ethanol solution

On the basis of our understanding of the lack of amphiphile aggregation in two-component low dielectric systems, we now study the aggregation phenomenon for the three-component systems and the microemulsion formation process. As in the general understanding of the microemulsion formation in aqueous systems, microemulsions are produced from aggregates of surfactant micelles. Does the lack of PAE aggregation in ethanol mean no microemulsion formation? Study of the three component systems should give us the answer to this question, and a helpful understanding of multi-component low dielectric systems as well.

To do this, we gradually added *n*-hexadecane to the PPG3M/ethanol solution obtained above and monitored the change in fluorescence peak III/I ratio of pyrene in the system. The result is shown in Figure 4.3.2.1. Surprisingly, as seen in the diagram, once n-hexadecane was added to the PPG3M/ethanol solution, the III/I ratio of pyrene increased, and continued to rise as the concentration of PPG3M increased in the system, reaching about 1.1 at high v/v % of *n*-hexadecane/ethanol. This indicates a hydrocarbon microenvironment formed, that is, a non-aqueous microemulsion of *n*-hexadecane-in-ethanol was produced. The III/I ratio we obtained here is close to or larger than that of Zana et al (3) for aqueous systems. From this study, we can see that the formation of oil-in-solvent microemulsion in the low dielectric systems is a continuous process, that oil is an indispensable component in the system, and the microemulsion formation is a result of the interaction of all three components.

To further observe and confirm this finding and the corresponding explanation of the non-aqueous microemulsion formation in ethanol, we studied the effect of *n*–

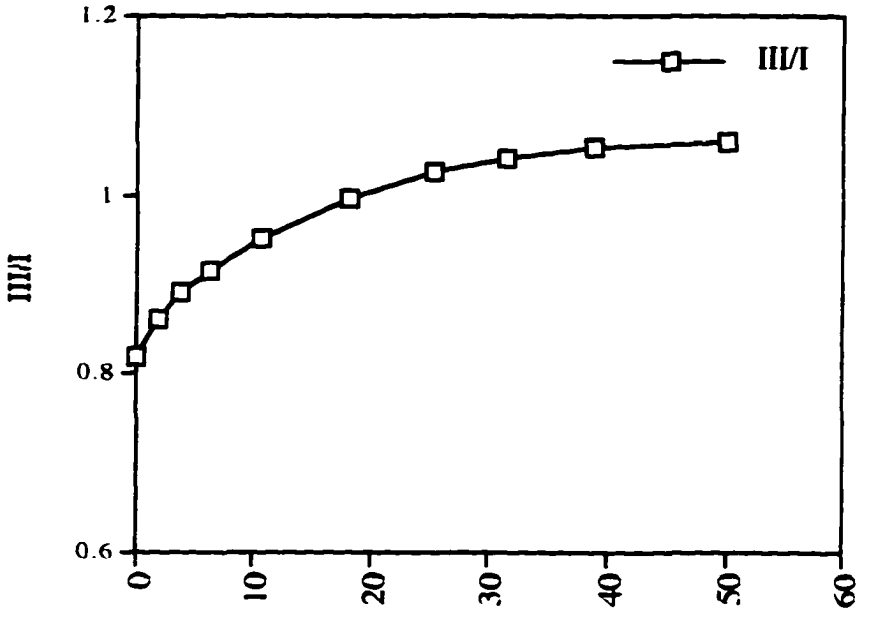


Figure 4.3.2.1 Fluorescence Peak III/I Ratio of Pyrene as Function of *n*-Hexadecane Added to the PPP3M/Ethanol Solution Obtained in Figure 4.3.1.2.

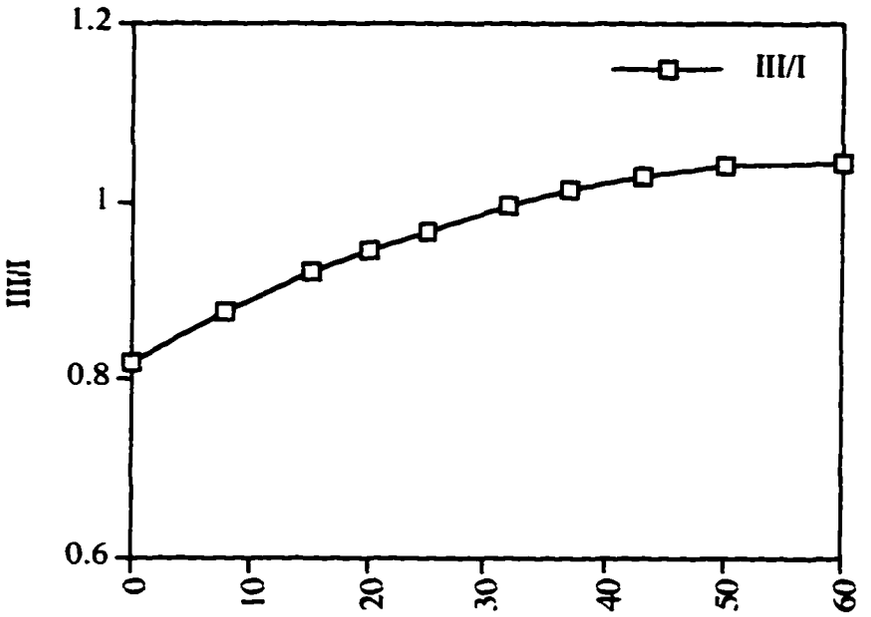


Figure 4.3.2.2 Fluorescence Peak III/I Ratio of Pyrene as Function of *n*-Hexadecane Added to the PPP10C/Ethanol Solution Obtained in Figure 4.3.1.3.

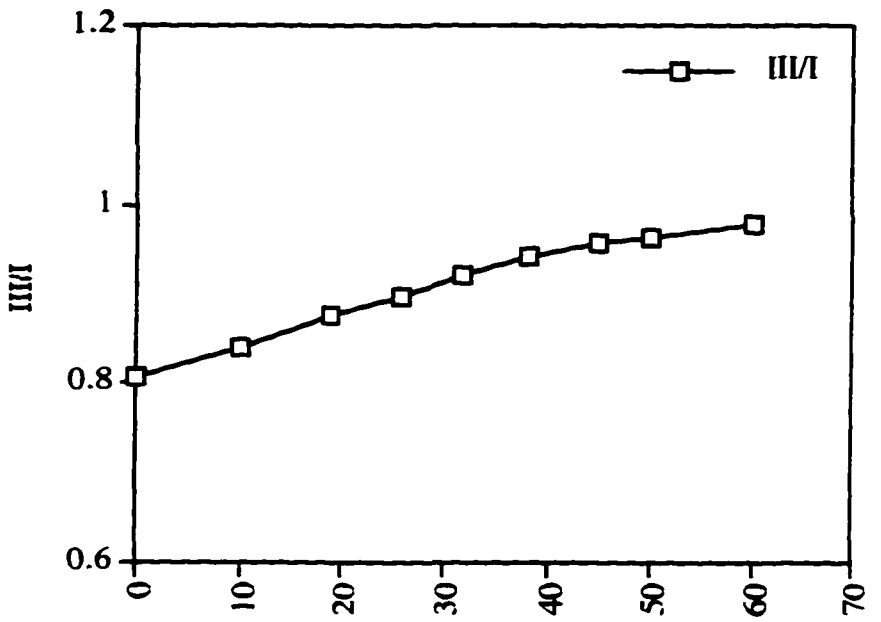


Figure 4.3.2.3 Fluorescence Peak III/I Ratio of Pyrene as Function of *n*-Hexadecane Added to the PPP30C/Ethanol Solution Obtained in Figure 4.3.1.4.

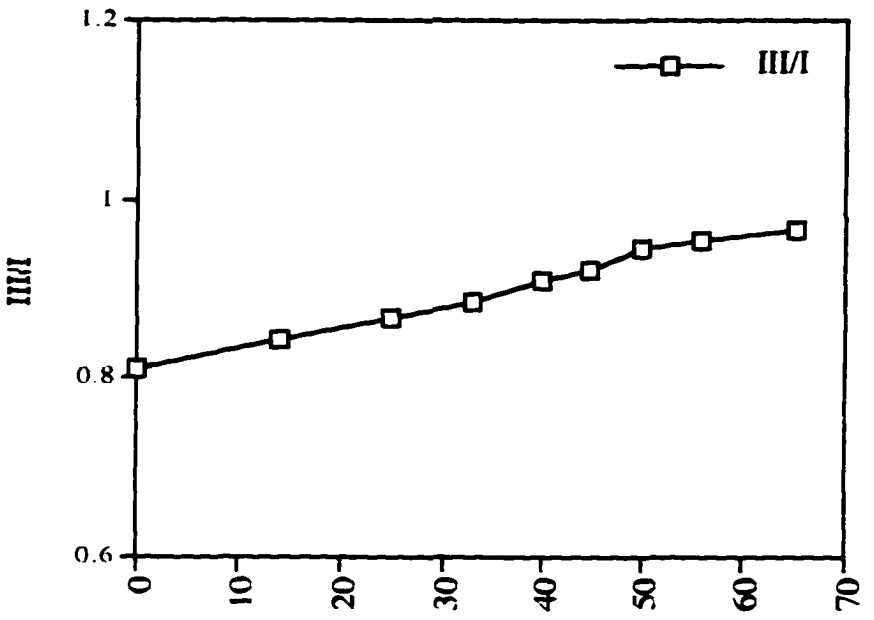


Figure 4.3.2.4 Fluorescence Peak III/I Ratio of Pyrene as Function of *n*-Hexadecane Added to the PPP50C/Ethanol Solution Obtained in Figure 4.3.1.5.

hexadecane addition on the aggregation behavior in PAE/ethanol solution with PPG10C, PPG30C and PPG50C by monitoring the III/I ratio change. The results are shown in Figure 4.3.2.2, Figure 4.3.2.3 and Figure 4.3.2.4, respectively. The results show again the gradual increase of III/I ratio as the concentration of PAE increases, indicating a gradual formation of *n*-hexadecane-in-ethanol microemulsion from corresponding PAE/ethanol solutions. This enhances our understanding of the microemulsion formation process above.

Another fact we may notice here is that the increase of the pyrene III/I ratio in PAE series slows down as the number of PPG units in the amphiphile's polar head increases from three in PPG3M to fifty in PPG50C (if we compare the III/I ratio changes for all four amphiphiles), indicating a gradual, loose, interfacial structure for the pyrene molecule to travel and experience. This is expected and is in parallel with the results from our monolayer experiment, computer modeling (Figure 3.3.4c) and H^1-NMR (next chapter), because a longer PPG chain in the PAE molecule tends to form a larger head group, and thus make the interfacial layer much less compact and more penetrable to ethanol or *n*-hexadecane molecules.

Pyrene Lifetime Measurement in n-Hexadecane-in-Ethanol non-aqueous Microemulsions

Although much less used in literature, another important feature of pyrene molecule fluorescence we can utilize to study the aggregation in microemulsions is the lifetime of its excited state, which is sensitive to the polarity in the microenvironment it senses. Based on this, we made lifetime measurements on typical *n*-hexadecane-in-ethanol microemulsions, and the results are shown in Table 4.3.2. The table shows that there is a large difference in lifetime between ethanol solution (370 ns) (13, 14) and *n*-hexadecane solution (290 ns) and that the lifetimes measured on microemulsion samples are close to that on *n*-hexadecane, indicating a hydrocarbon microenvironment formed. This is in parallel with our results discussed above.

Table 4.3.2 Pyrene Lifetime Measurement in *n*-Hexadecane-in-Ethanol Non-aqueous Microemulsions

(pyrene concentration in samples: $10^{-7}M$)

Pyrene environment	Pure *n*-$C_{16}H_{34}$	*n*-$C_{16}H_{34}$/ PPG3M/EtOH	*n*-$C_{16}H_{34}$/ PPG10C/EtOH	Pure EtOH
Lifetime, *ns*	290	288	285	370

4.3.3 PAE aggregation behavior in *n*-hexadecane

To understand the formation of ethanol-in-*n*-hexadecane non-aqueous microemulsion, we began our study with an amphiphile/*n*-hexadecane two-component system first, as we did in the study of ethanol-in-*n*-hexadecane microemulsion above. We used pyrene-1-carboxaldehyde as the structural probe because of its amphiphilic structural feature and the sensitive change of its fluorescence maximum with the dielectric constant of the medium and the formation of an interfacial layer (2, 6, 10, 15).

Figure 4.3.3.1 shows typical results for the amphiphile/*n*-hexadecane two-component systems using PPG3M. As we can observe from the diagram, there was no fluorescence maximum shift, indicating no change in local polarity, and no formation of amphiphile interfacial layer or aggregates similar to reversed micelles.

To confirm this observation, we also carried out fluorescence measurements on PPG10C, PPG30C and PPG50C/ethanol systems, and similar results were obtained (see Figure 4.3.3.2).

The systematic observation of the series of polyoxypropylene alkyl ethers in *n*-hexadecane confirms that, unlike regular surfactant/oil micellar systems, amphiphiles like polyoxypropylene alkyl ethers do not form micelles or aggregates in oil.

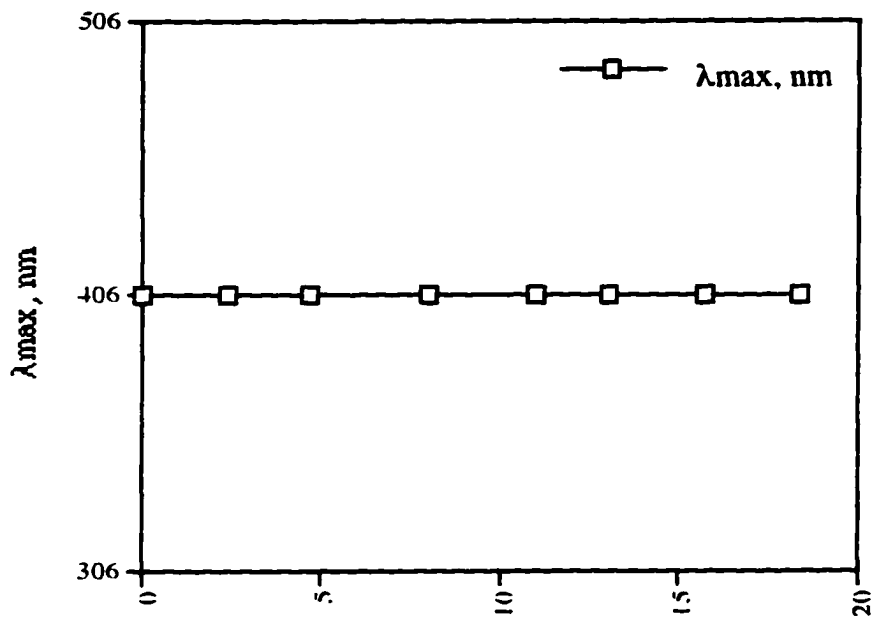


Figure 4.3.3.1 Fluorescence λmax of Pyrene-1-Carboxaldehyde ($2x10^{-5}M$) in n-Hexadecane/PPG3M Solution as Function of PPG3M Concentration.

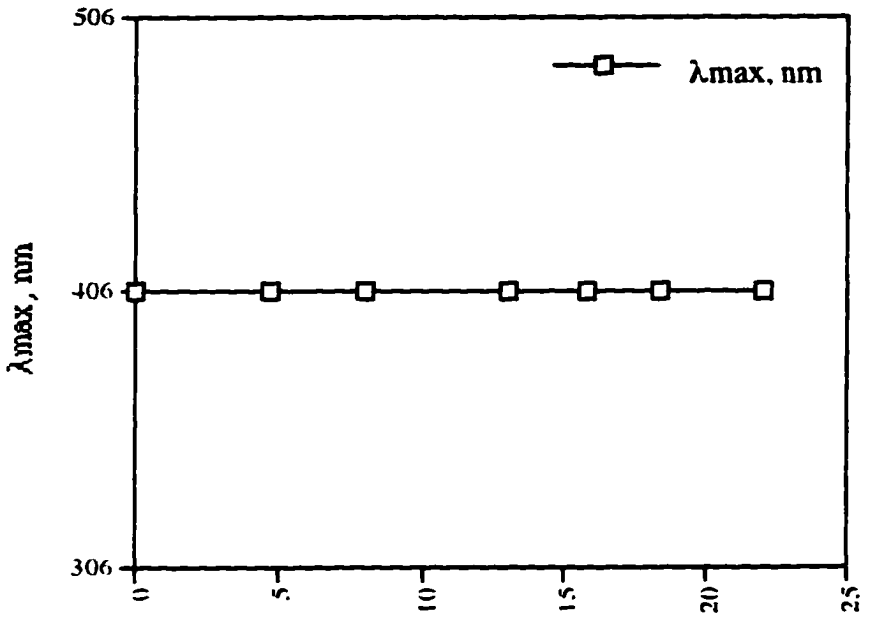


Figure 4.3.3.2 Fluorescence λmax of Pyrene-1-Carboxaldehyde ($2x10^{-5}M$) in n-Hexadecane/PPG10C Solution as Function of PPG10C Concentration.

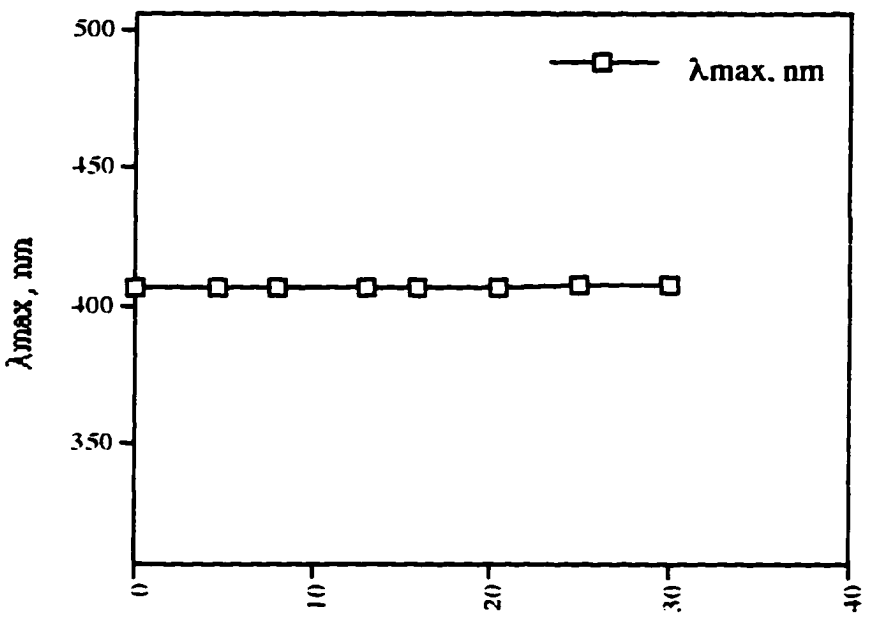


Figure 4.3.3.3 Fluorescence λmax of Pyrene-1-Carboxaldehyde ($2x10^{-5}M$) in n-Hexadecane/PPG30C Solution as Function of PPG30C Concentration.

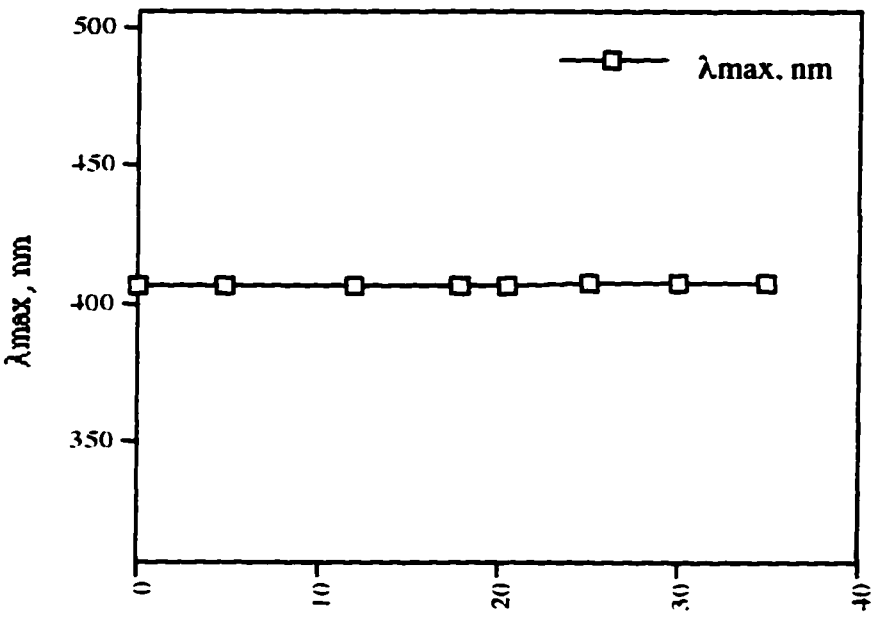


Figure 4.3.3.4 Fluorescence λmax of Pyrene-1-Carboxaldehyde ($2x10^{-5}M$) in n-Hexadecane/PPG50C Solution as Function of PPG50C Concentration.

4.3.4 Effect of ethanol addition on the aggregation behavior in PAE/*n*-hexadecane solution

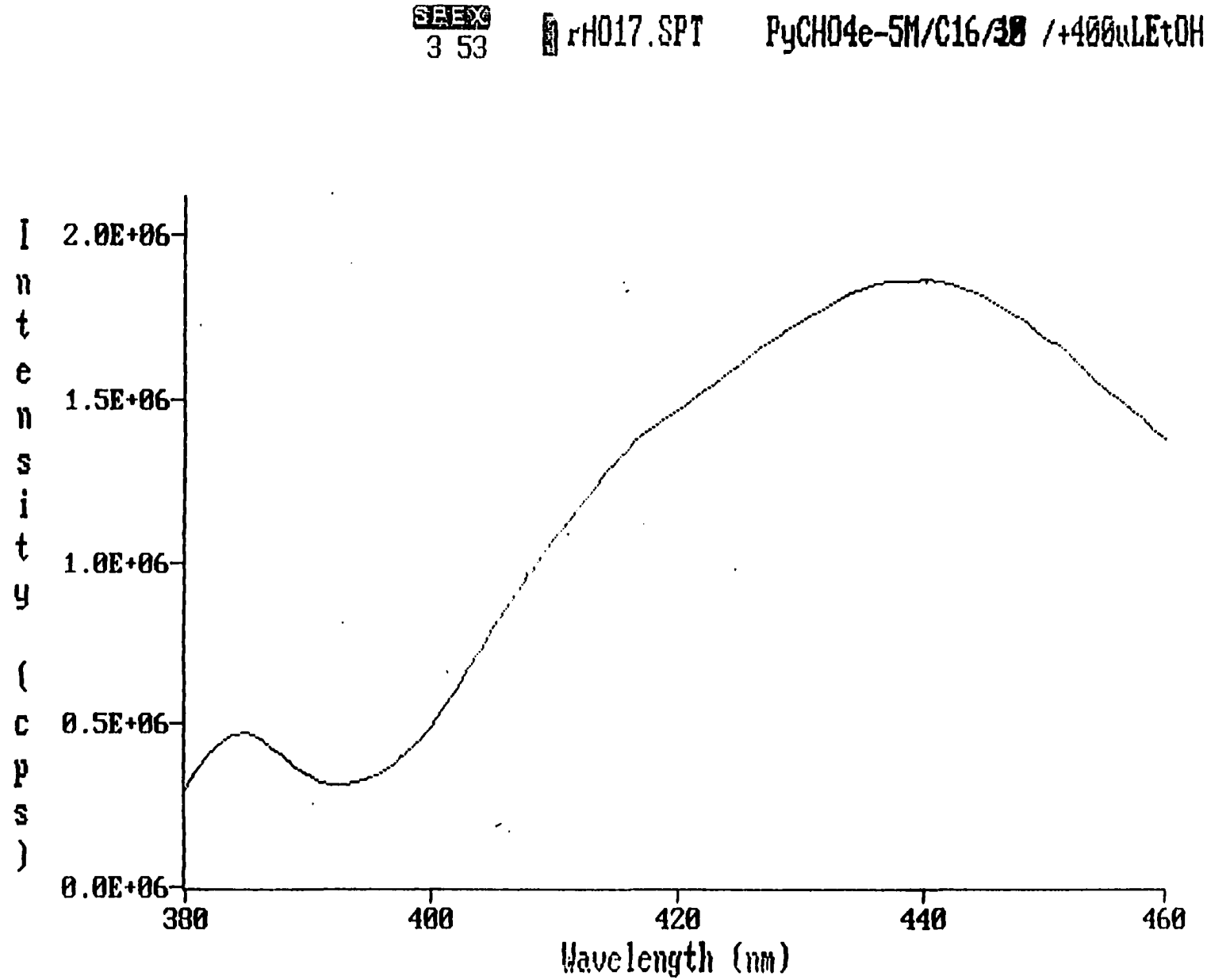
Given the absence of amphiphile aggregation in PAE/*n*-hexadecane two component systems, we next studied the aggregation phenomenon for the three component systems and the formation process of ethanol-in-*n*-hexadecane microemulsion. As the general understanding of the microemulsion formation in aqueous systems, this type of microemulsion is produced from aggregates of reversed surfactant micelles. Does the lack of PAE aggregation in *n*-hexadecane mean no microemulsion formation? Study of the three component systems should give us the answer to the question.

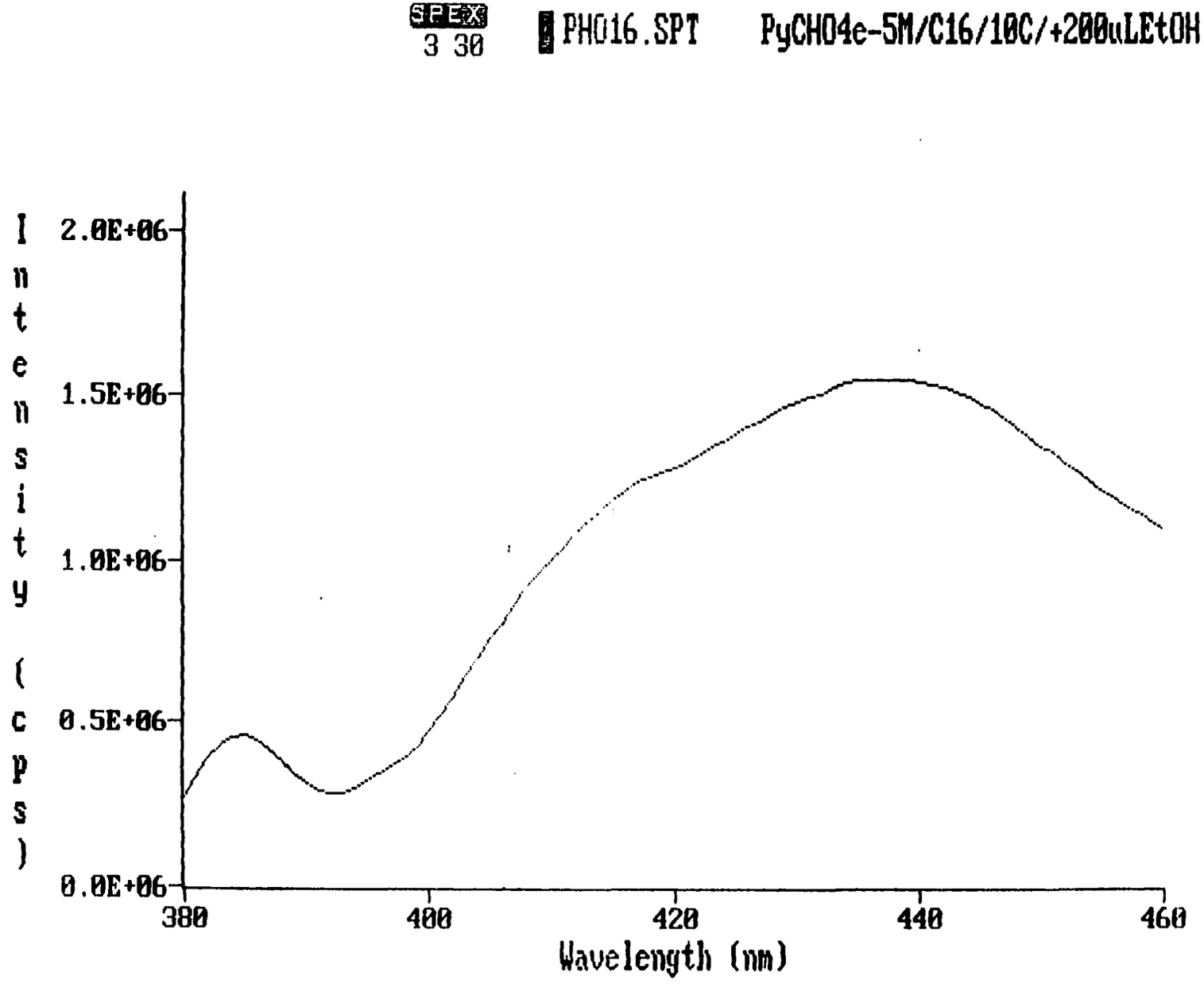
As in the case of adding *n*-hexadecane to PAE/ethanol solutions, addition of ethanol to PAE/*n*-hexadecane solutions caused continuous fluorescence λ_{max} shifts in the long wavelength direction, indicating a more polar microenvironment similar to ethanol is gradually formed. A typical result with PPG3M/*n*-hexadecane is shown in Figure 4.3.4.1.

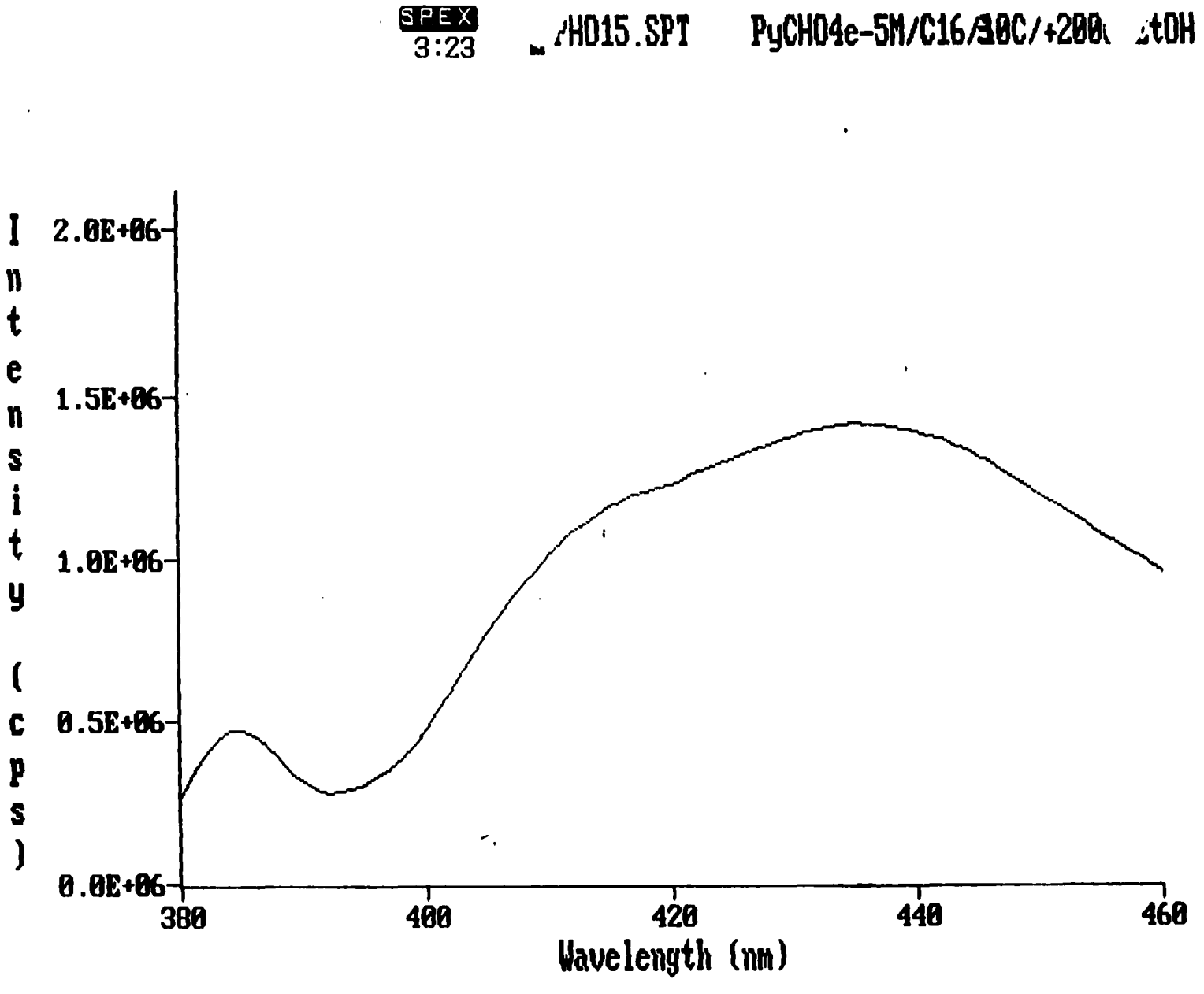
To confirm this observation, we further carried out fluorescence measurements on PPG10C, PPG30C and PPG50C/ethanol systems, and similar results were obtained (see figures below).

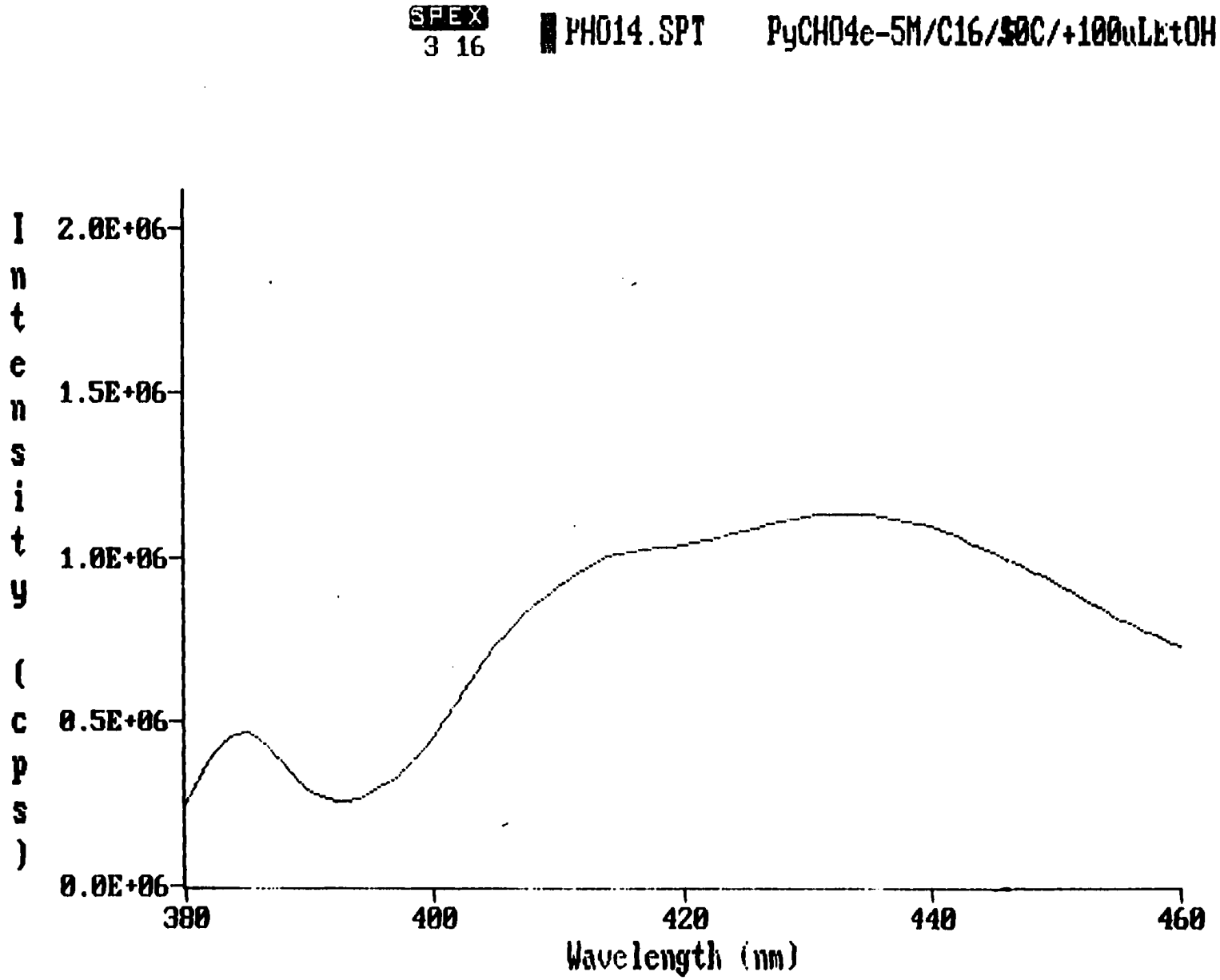
The systematic observation of the series of polyoxypropylene alkyl ethers confirms the formation of ethanol-in-*n*-hexadecane microemulsion, and that the process is gradual and continuous.

Figure 4.3.4.1 Typical Pyrene-1-carboxaldehyde Fluorescence Spectra of PAE/*n*-hexadecane Solutions Containing Added Ethanol.









4.4 Summary

In this chapter, we have systematically studied polyoxypropylene alkyl ether aggregation in both ethanol and *n*-hexadecane, and the formation of both *n*-hexadecane-in-ethanol and ethanol-in-*n*-hexadecane microemulsions using the fluorescence probe technique. We have found that polyoxypropylene alkyl ethers do not aggregate either in ethanol or in *n*-hexadecane. We also found that the formation of microemulsions is a result of the interaction of all three components in the system, and the formation process is gradual and continuous, from two-component solution to three-component aggregation. All these are dramatically different from aqueous systems. The results and understanding obtained here offer us hints for the study of other non-aqueous and low dielectric systems.

4.5 References

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Chapter 5

Structural Aspects and Other Properties of Ethanol/*n*-Hexadecane Non-aqueous Microemulsion Systems

5.1 Introduction

In the previous chapters, we have reviewed and analyzed the literature in the area of non-aqueous media, and have identified the topic of non-aqueous microemulsions for low dielectric systems; we have approached the problem with various surfactants and failed. We have further studied the cosolubilization effect of polyoxypropylene (3) myristyl ether on the ethanol/oil pair, and found with a series of polyoxypropylene alkyl ethers that we could successfully prepare and identify non-aqueous microemulsions for the low dielectric systems. We have also conducted a systematic investigation of the microemulsion formation processes and understood some of the special features of the formation of non-aqueous microemulsions of low dielectric systems.

On the basis of these studies, we now want to examine and explore the structural aspects, and the properties, of the microemulsion systems we made, and try to link them to the formation process.

To do this in an orderly way, we will first study the changes in the polar subphase and their effects on the systems, and then the changes in the non-polar subphase and their effects. Finally, we will focus our attention on the interfacial region and the structure and properties of the microemulsifier, and answer the question of why this series of microemulsifiers can form non-aqueous microemulsions with ethanol and *n*-hexadecane.

5.2 Experimental

Materials

PPG3M, PPG10C, PPG30C and PPG50C. Same as in Chapter 3.

PPG14B, PPG10DB and PPG5/PEG20C. Croda gifts. They have structures as following:

PPG14B: Polyoxypropylene (14) butyl ether: n-$C_4H_{10}O(CH_2CHCH_3O)_{14}H$

PPG10DB: Polyoxypropylene (10) butyl ether: $(n\text{-}C_4H_{10}O)_2(CH_2CHCH_3O)_{10}$

PPG5/PEG20C: Polyoxypropylene (5) polyoxyethylene (20) cetyl ether:

n-$C_{16}H_{30}O(CH_2CH_2O)_{20}(CH_2CHCH_3O)_5H$

PPG425, PPG725, PPG1000, PPG2000, PPG3000 and PPG4000. From Aldrich. The number in the name indicates molecular weight. They have structures as following:

$$HO(CH_2CHCH_3O)_nH$$

PEG400, PEG600, PEG900. From Aldrich. The number in the name indicates molecular weight. They have structures as following:

$$HOCH_2CH_2O)_nH$$

Z150, Z300,1GS, 3GS and 4GS. Same as in Chapter 2.

Titration

Same as in chapter 3.

NMR

H^1-NMR spectra were taken on a 300 MHz IBM instrument, using 5 mm tube for sampling.

Computer modeling

Same as in Chapter 3.

5.3 Results and Discussions

5.3.1 Effects of water

The first important factor we examined was water. As we summarized in chapter one, water is an indispensable component for the formation of some microemulsions, especially for the glycol and diol systems; this has been seen from Winsor and others' work (1, 2, 3, 4, 5, 6). Because our microemulsion preparations were carried out under ambient atmosphere, there inevitably existed some trace amount of water in the microemulsion systems obtained. Whether this trace amount of water plays a major role in the formation of these systems is crucial, and the key to differentiate a true non-aqueous microemulsion from the water-solvent hybrid microemulsions.

Effect of Trace Amounts of Water from Air

To study the effect of the moisture from ambient atmosphere, we first thoroughly dried extensively the closed, clear mixtures obtained by titration of minimum amounts of the series of polyoxypropylene alkyl ether microemulsifiers with various drying agents:

Molecular sieve 3Å

Drierite (anhydrous $CaSO_4$)

Phosphorous Pentoxide (P_2O_5)

The systems remained clear and stable and the electric resistance did not change noticeably. The systems remained stable.

For the formation process, we then used materials which were all pre-dried with the drying agents above to do the titration and the results showed no noticeable difference in amounts of microemulsifiers used (this has been done for all four polyoxypropylene alkyl ethers).

These results showed that the trace amount of water from air has no effect on the formation of ethanol/polyoxypropylene alkyl ether/*n*-hexadecane microemulsion systems.

Effect of Much Larger Amounts of Water

To further study the effect of water on the microemulsion systems we found, we next intentionally added a certain amount of water to the system to observe its effect on the formation process; typical results are shown with microemulsifier PPG3M in Table 5.3.1.

From the table, we see the minimum amount of microemulsifier required increases very quickly as the amount of water in the system increases, making the final product more structurally similar to a molecular solution instead of microemulsion. Also, we observed that mixtures above (containing added water) separated **faster** than those without water added at near-clear points during titration; this can be explained by the increased intermolecular attraction between polar molecules due to adding a more polar solvent (water) into the polar subphase.

These results show that unlike polar solvent/water hybrid microemulsions studied in the literature, water here is not a necessary component and makes no contribution to the formation of the interface of the non-aqueous microemulsions, but rather requires a larger amount of microemulsifier to clarify the system.

Table 5.3.1 Effect of Much Larger Amount of Water

The Minimum Amounts of PPG3M Required to Clarify

n-$C_{16}H_{34}$/EtOH/H_2O Mixtures

(*n*-$C_{16}H_{34}$+EtOH+H_2O =100. EtOH+H_2O=50, by volume before titration)

Amount of Water Added	Amount of PPG3M Required
0	9%
0.1%	12%
1%	16%
5%	29%

5.3.2 Effect of poorer solvents

The next important factor we examined from the polar subphase side was poorer solvents, that is, polar solvents with a dielectric constant larger than that for ethanol. Poorer solvents are useful variables in changing the polar subphase in the microemulsion systems for various applications. To study the effect of poorer solvents on the formation of the non-aqueous microemulsions we found, we intentionally added certain amounts of these polar liquids to the system to observe their behavior towards the formation process: the typical results with microemulsifier PPG3M are listed against the dielectric constant of the solvent in Table 5.3.2.

From the table, we see the minimum amount of microemulsifier required increases very quickly as the dielectric constant of the solvent increases, making the final product more structurally similar to a molecular solution instead of microemulsion. We also observed that these mixtures (containing added polar liquid) separated **faster** than those without polar liquid added at near-clear points during titration; this can be explained by the increased intermolecular attraction between polar molecules due to adding more polar solvent into the polar subphase. These features were observed for all four microemulsifier systems.

Poorer solvents, such as glycerol, have been added to the polar subphase, such as propylene glycol, to form non-aqueous microemulsions where the microemulsifier has been polyoxyethylene alkyl ethers (7, 8). In those systems, glycerol addition is necessary. Comparatively, the results in Table 5.3.2 show that poorer solvents are not necessary for the formation of our non-aqueous microemulsion systems. This can be understood from our previous findings (Chapter 2) that surfactants containing polyoxyethylene units are not suitable for making microemulsions with low dielectric systems. The polyoxyethylated

Table 5.3.2 Effect of Poorer Solvents

The Minimum Amounts of PPG3M Required to Clarify

n-$C_{16}H_{34}$/EtOH/Solvent Mixtures

(*n*-$C_{16}H_{34}$+EtOH+Solvent=100, EtOH=solvent=25, by volume before titration)

Solvent Added	ε	Amount of PPG3M Required
none		9%
Methanol	31.2	25%
Propylene Glycol	32.0	26%
Glycol	37.7	>100%
Glycerol	42.5	>300%

chains in the surfactants are more polar than polyoxypropylene units in polyoxypropylene alkyl ethers. The presence of methyl groups in polyoxypropylene alkyl ethers make the polar head group less polar and more flexible, and therefore suitable for solvents with lower dielectric, such as ethanol. This is also supported by the results from our NMR and frozen experiments (later in this chapter).

These results show that poorer solvents, with a larger value of dielectric constant, once added to ethanol, do not help the formation of the interface or non-aqueous microemulsions, but rather require a larger amount of microemulsifier to clarify the system, or make it actually impossible to form microemulsions.

5.3.3 Effect of oil change

After studying the effects from the polar subphase side, we next consider the effects from the oil subphase. Change in the oil subphase in a microemulsion system is useful for various applications. To observe the effect of other oils on the formation of the non-aqueous microemulsions we prepared, we intentionally added certain amounts of these non-polar liquids to the system to observe their effect on the formation process; the typical results with microemulsifier PPG3M and PPG10C are listed against the molecular weight and viscosity of the oil in Table 5.3.3.

From the table, we see that the minimum amount of microemulsifiers required increases very quickly as the molecular weight or viscosity of the added oil (within same type) increases, making the oil/ethanol mixture more difficult to clarify and the microemulsifier less efficient in terms of forming microemulsions. This is expected because, as the molecular weight increases, the attraction between oil molecules increases and therefore the non-polar component tends to hold more strongly together, and become less permeant to the hydrocarbon chain in the amphiphile molecules; thus it requires a larger amount of polyoxypropylene alkyl ethers to break down the non-polar bulk phase and increase its surface area and interaction with the amphiphile.

From the table, we also see that polyoxypropylene alkyl ethers can form microemulsions with various industrial oils with reasonable quantities, and this is good for practical applications.

Table 5.3.3 Effect of Oil Change

The Minimum Amounts of Microemulsifiers Required to Clarify Oil/EtOH Mixtures

(Oil+EtOH=100, EtOH=Oil=50, by volume before titration)

Oil	M.W. or Viscosity	PPG3M	PPG10C
n-Hexadecane	226.5	9%	10%
Z150	334	3%	3%
Z300	372	4%	5%
1GS	25.0cSt/100°F	14%	15%
3GS	33.0cSt/100°F	18%	20%
4GS	62.5cSt/100°F	20%	26%

5.3.4 The structure and properties of polyoxypropylene alkyl ethers and the formation of ethanol/*n*-hexadecane microemulsion systems

After studying the effects from both the non-polar and polar subphases, we now turn our attention to the properties and structural features of the microemulsifier, and their contribution to the formation of the interfacial region in our non-aqueous microemulsion systems.

The role of the polyoxypropylene alkyl ether series in microemulsification of ethanol/*n*-hexadecane mixture is unique if we consider the failure of all surfactants we studied for low dielectric systems before. Naturally, we have asked ourselves the following question:

Why can the series of polyoxypropylene alkyl ethers form microemulsions with ethanol/n-hexadecane?

To answer the question, we began by studying the solubility of the amphiphile, because this class of molecules is new and little is known about its properties. Table 5.3.4.1 shows the solubilities of these amphiphiles in *n*-hexadecane, ethanol and water. From the table, these molecules are soluble both in ethanol and in *n*-hexadecane, and this makes them easily movable and arrangeable in the interfacial region. However, they are not soluble in water at room temperature. This is somewhat surprising and is probably due to the low polarity of the polyoxypropylene chain. Actually, a further test on the polar component of these amphiphiles shows that even the polar polypropylene glycol (PPG) chain itself is not soluble in water (see Table 5.3.4.2). This low polarity of the polar chain comes from the presence of the methyl group in the structure. Compared to them, polyethylene glycols (PEGs), which are soluble in water at room temperature and are the polar component in the non-ionic surfactant polyoxyethylene alkyl ethers, are more polar.

Table 5.3.4.1 Solubility of Microemulsifiers in *n*-$C_{16}H_{34}$, in EtOH and in H_2O at 25°C

	in *n*-$C_{16}H_{34}$	in EtOH	in H_2O
PPG3M	soluble	soluble	not soluble
PPG10C	soluble	soluble	not soluble
PPG30C	soluble	soluble	not soluble
PPG50C	soluble	soluble	not soluble

Table 5.3.4.2 Solubility of the Polar Component of the Microemulsifier in EtOH and in H_2O at 25°C

	in EtOH	in H_2O
PPG425	soluble	soluble
PPG725	soluble	not soluble
PPG1000	soluble	not soluble
PPG2000	soluble	not soluble
PPG3000	soluble	not soluble
PPG4000	soluble	not soluble

To further understand the structural effect of the polar PPG chain on the formation of the microemulsion systems, we studied the hydrogen bonding interaction between ethanol and PPG molecules by H^1-NMR . We monitored the chemical shift of the proton in the OH group of ethanol, because this proton is the only active proton in the system and the value of its chemical shift indicates the strength of hydrogen bonding in the system. The NMR results are shown in Figures 5.3.4.1.

From the figure, the chemical shift of the proton decreases as the concentration of PPG molecule increases, indicating that polypropylene glycol molecules can effectively penetrate into the ethanol phase and the hydrogen bonding which existed in the liquid ethanol is broken down and replaced partially by the hydrogen bonding interaction between the ethanol proton and the ether oxygen in polypropylene glycol. This interaction contributes to the interface formed by polyoxypropylene alkyl ethers in the ethanol/*n*-hexadecane non-aqueous microemulsions.

We also notice that the addition of PPG molecules causes the proton peak to shift to smaller values (not to larger values). This is because of the increasing non-polar interaction between hydrocarbon groups of both ethanol and PPG molecules, due to the presence of the methyl group in the PPG chain. The presence of the methyl group weakens the attractive interaction between the PPG chains and offers space for ethanol molecules to stay and interact with the chain; this also contributes to the formation of the interfacial layer and corresponding microemulsions. Our computer modeling shows parallel results. As shown typically in the Figure 5.3.4.2, the ethanol molecules can fit suitably in the space formed by the PPG chain and interact effectively with it.

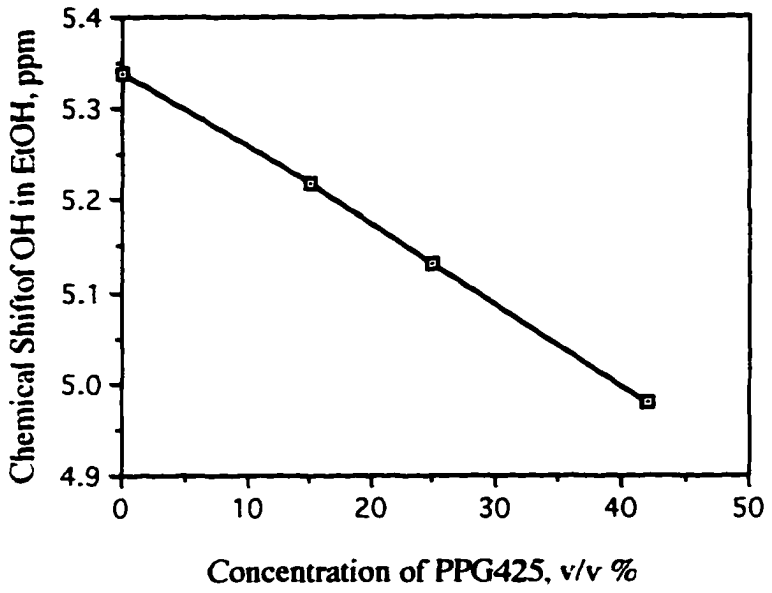


Figure 5.3.4.1 H^1-NMR Chemical Shift of OH in Ethanol vs. the Concentration of PPG425 Added.

ETHANOL: PPG425

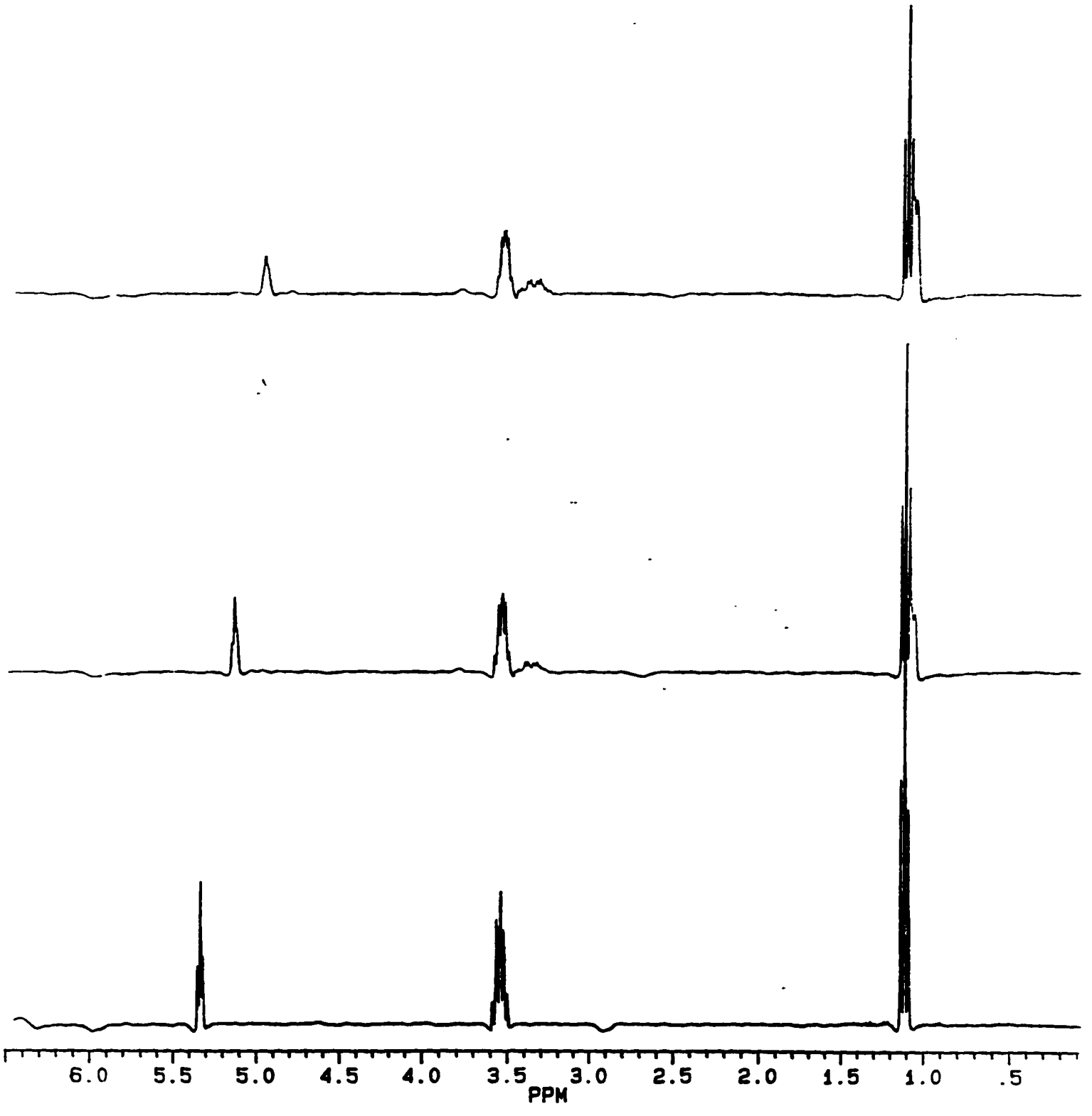
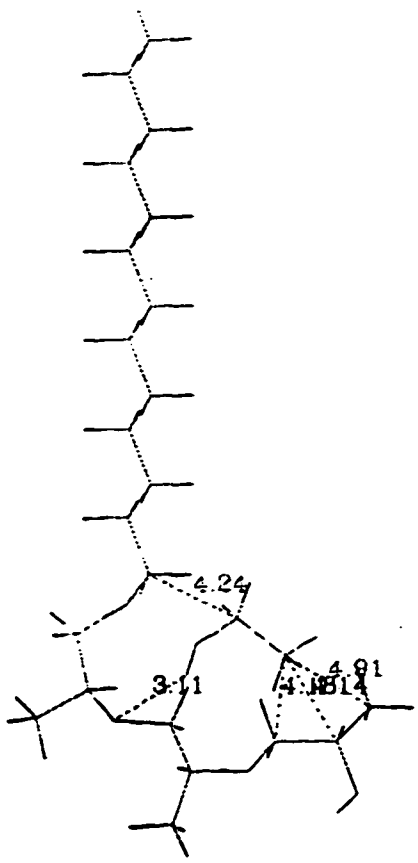


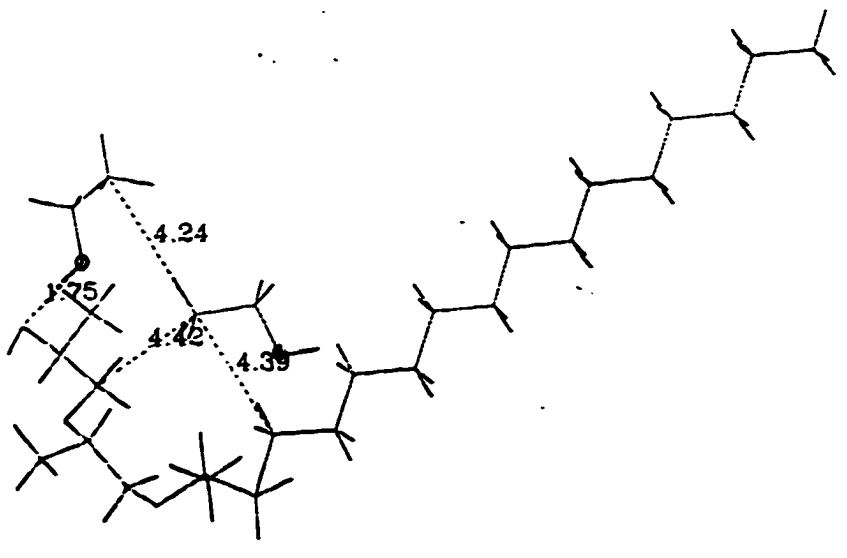
Figure 5.3.4.2 Computer modeling of ethanol/polyoxypropylene alkyl ether systems.

(Ethanol molecules are highlighted. Shown here are typical results. After energy minimization, ethanol molecules can fit suitably in the space formed by the PPG chain of the amphiphiles.)

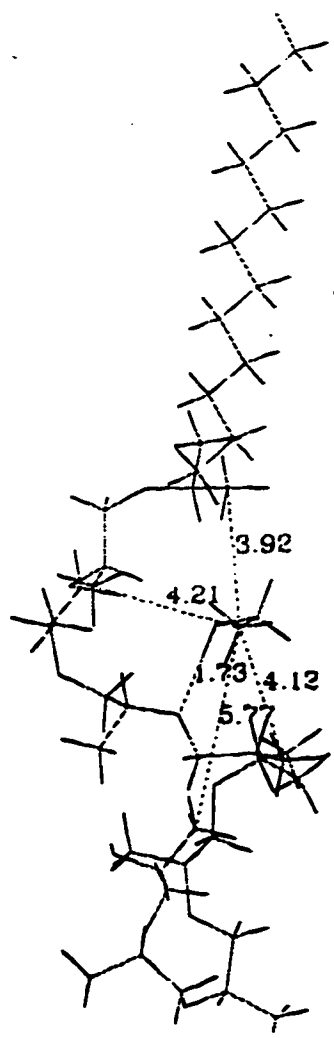
PPG3M+1 EtOH



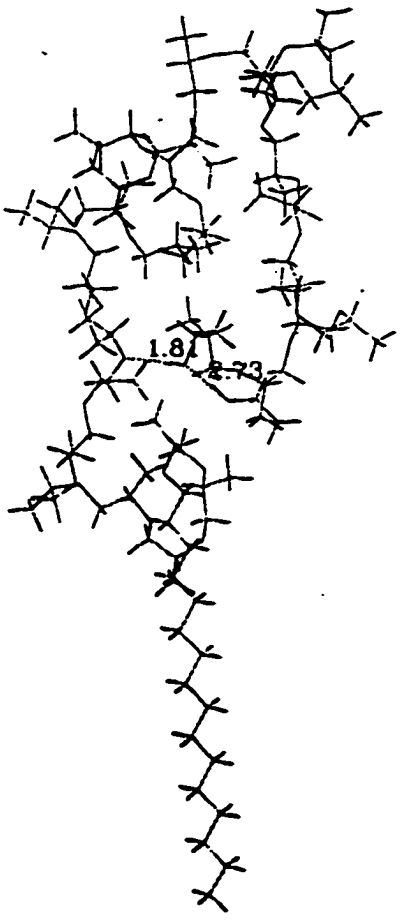
PPG3M+2 EtOH



PPG10C+1 EtOH



PPG30C + 1 EtOH



The effect of the presence of the methyl group on the polar chain can be also seen from the low temperature behavior of PEG and PPG molecules, as shown in Table 5.3.4.3. From the experiment, we see that the attraction between polar chains is greatly weakened by the presence of the methyl group, making the PPG chains not frozen even at dry ice (-77°C) temperature .

Table 5.3.4.3 Low Temperature Behavior of PEG & PPG Molecules

Molecule	Temperature	Phase Behavior
PPG425	-77°C	liquid
PPG725	-77°C	liquid
PEG400	-10°C	solid
PEG600	-10°C	solid
PEG900	-10°C	solid

Existence of the methyl side group in long chain molecules weakens attraction between chains.

The roles of the methyl group in the microemulsifier

Overall, as discussed above, the presence of the methyl group in the microemulsifier plays the following roles in the formation of the interfacial region and therefore the ethanol/*n*-hexadecane non-aqueous microemulsion systems:

—weakening interaction between PPG chains;

—offering space for ethanol molecules to stay;

—lowering the polarity of the chain enough for **effective** interaction with ethanol to form the interfacial region for microemulsions.

We also studied the effect of the structural changes in the components of the microemulsifier on the formation of ethanol/*n*-hexadecane microemulsion systems: the results are shown in Table 5.3.4.4.

The table shows, along with the change in the polar chain, that it requires a much larger amount of microemulsifier to clarify the ethanol/*n*-hexadecane mixture during titration when PPG5/PEG20C is used as the microemulsifier. PPG5/PEG20C is structurally similar to PPG30C, except for lack of some methyl groups in its polar chain. The results show again the important and unique roles of the presence of the methyl group in the polar chain, as discussed above.

On the other side, along the hydrocarbon chain, the table shows that shortening in hydrocarbon chain length to four units in PPG14B requires a much greater amount of amphiphile to clarify the ethanol/n-hexadecane mixture during titration, making the system more like solution (molecular dispersion). The same situation was observed for the PPG10DB system; here the concentration of the hydrocarbon chain has been doubled but the length has stayed the same. These results are expected because a common requirement for surfactants to form aggregates in liquids is that their hydrocarbon chain should be

Table 5.4.3.4 Effects of the Component Structures of the Microemulsifier on the Formation of EtOH/*n*-$C_{16}H_{34}$ Microemulsions

Change in the polar part:	
PPG5/PEG20C	requires **much larger** amounts (>100%v/v) to clarify the EtOH/ *n*-$C_{16}H_{34}$ mixtures during titration
Change in the non-polar part:	
PPG14B PPG10DB	requires **much larger** amounts (>100%v/v) to clarify the EtOH/ *n*-$C_{16}H_{34}$ mixtures during titration

longer than 10 units. The longer hydrocarbon chain in PPG3M, PPG10C, PPG30C and PPG50C make them tend to hold together and effectively interact with the oil molecules, which can also been seen in our computer modeling results, as shown in the Figure 5.3.4.3.

After the above studies, we now can answer the question of why the series of polyoxypropylene alkyl ethers can uniquely and effectively form the interfacial layer and thus non-aqueous microemulsions with ethanol and *n*-hexadecane with the following observations:

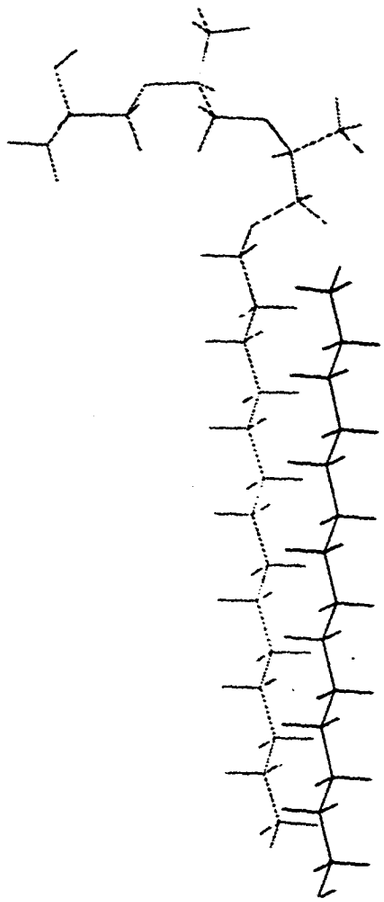
----they are of moderate polarity and suitable structure in their hydrophilic part;

----they of are moderate length in their hydrocarbon chain.

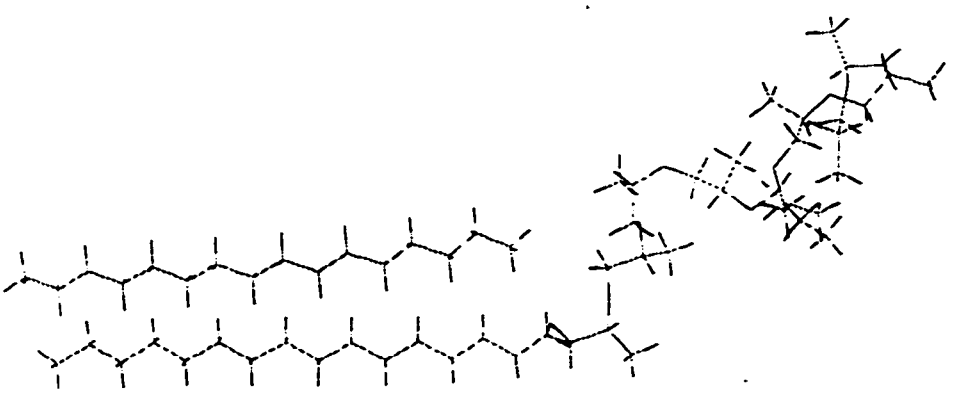
Figure 5.3.4.3 Computer modeling of *n*-hexadecane/polyoxypropylene alkyl ether systems.

(After energy minimization, the hydrocarbon was found to line up in the all-trans configuration with the hydrophobic tail of the amphiphile, as expected.)

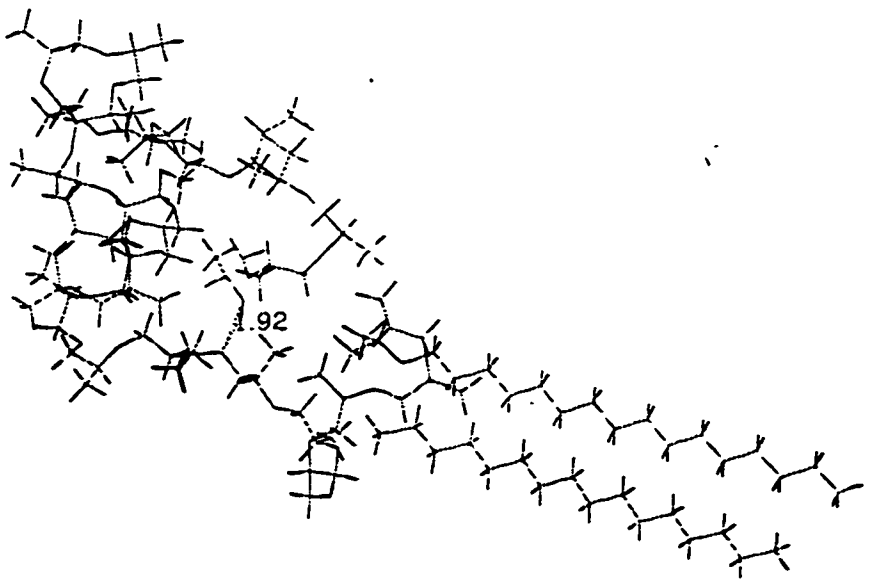
PPG3M+nC16H34



PPG10C+nC16H34



PPG30C+nC16H34



5.4 Summary

In this chapter, we have examined the effects of the structural and other properties on the formation of ethanol/*n*-hexadecane non-aqueous microemulsion systems from the polar subphase, the non-polar subphase and the interfacial region side. We have found that water is not a necessary component for the formation of the interfacial layer and addition of poorer solvents has an adverse influence on the formation of these non-aqueous microemulsions. Also, we have showed and explained the unique roles of the methyl group present in the polyoxypropylene alkyl ether amphiphile in microemulsification. Finally, we have studied the structural changes in both the polar and the hydrocarbon chain of the microemulsifier and have come to an understanding why this series of molecules can form non-aqueous microemulsions with ethanol/*n*-hexadecane.

5.5 References

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Conclusions

---The existence of non-aqueous micro-emulsions in low dielectric systems has been demonstrated with ethanol/*n*-hexadecane model systems;

---The selection of the amphiphile molecule is crucial for the formation of such systems;

---Non-aqueous microemulsions can be prepared with only **one** amphiphile which simplifies the formation process;

---EtOH/*n*-$C_{16}H_{34}$ non-aqueous microemulsions of both O/W and W/O types have been successfully prepared with a series of polypropylene alkyl esters and confirmed;

---The type of EtOH/*n*-$C_{16}H_{34}$ microemulsions can be changed by altering the volumetric ratio of EtOH/*n*-$C_{16}H_{34}$;

---Longer PPG chains in the microemulsifier tend to form *n*-hexadecane-in-ethanol type microemulsions;

---Microemulsifiers having short PPG chains are more efficient for the preparation of EtOH/*n*-$C_{16}H_{34}$ non-aqueous microemulsions;

---Polyoxypropylene alkyl ethers do not form aggregates either in ethanol or in *n*-hexadecane;

----The formation of ethanol/polyoxypropylene alkyl ether/*n*-hexadecane non-aqueous microemulsion systems is a result of the interaction of all three components in the system, and the formation process is gradual and continuous, from two component solution to three component aggregation;

----Water does not contribute to the formation of these low dielectric non-aqueous microemulsions, contrary to its behavior in the hybrid microemulsion system;

----The methyl group in the PPG part of the microemulsifier plays a crucial role for the formation of EtOH/*n*-$C_{16}H_{34}$ non-aqueous microemulsion systems;

----Fluorescence lifetime measurement of probe molecules, such as pyrene, can be utilized to study the formation of microemulsions, if there is a large difference in lifetime between the polar and the non-polar subphases;

----The knowledge obtained here can be used for the study of microemulsions in other non-aqueous and low dielectric systems, and applied to practical problems.

Prospects

Many developments can be imagined with the microemulsion systems we found.

----as media for making mesoporous ceramic materials through metal alkoxides;

----as media for the study of organic reactions;

----as models for theoretical study of percolation;

----further microemulsion studies using other amphiphiles;

----further microemulsion studies with other low dielectric solvents.

Appendix

Surfactants not yielding an emulsion with acetonitrile/Z150

ALCOLAC CHEMICAL Corp.

-DV x C: Polymeric surfactant sulfate

-SIPON LT-6: TEA lauryl sulfate

-SIPOTERIC COB: Cocoamidopropyl betain

-SIPOTERIC 1304/1398: Cocoamphocarboxyglycimate

-AKYPO RLM 160N

-SIPEX JKB: Ammonium salt sulfate

-SIPEX EST 30: Sodium tidecth sulfate

-Sipromide 1500: Cocoamide DEA

ATOCHEM

-FORAFAC 1116: Polyfluoroalkyl betain

-FORAFAC 1183N: Amine oxide

-FORAFAC 1190: Acrylic polymer

-FORAFAC 1199: nonionic Acrylic polymer

B.A.S.F.

-PLURONIC L 43

-PLURONIC L 44

-PLURONIC L 62

-PLURONIC L 63

-PLURONIC L 121

-PLURONIC L 122

-PLURONIC 25 R 2

CALGON Corp.

- MERQUAT 100 Polyquaternium-6

CHEMICAL COMPANY ONYX

- BTC 1010, 1010E, and 50 USP
- AMMONYX CO, SO, CDO, CETAC, DME, MCO, and T.
- NEUTRONYX 560, 600, 605, 626, 640, and 675.
- MAPROFIX ES, ES1, ES2, ES3: sodium lauryl ether sulfide.

CRODA

- CROVOL A40: Polyoxyethylene (20) almond glycerides HLB=10
- CROVOL A70: Polyoxyethylene (60) almond glycerides HLB=15
- PROMYRISTYL PM-3: Polyoxypropylene (3) myristyl ether
- POLYCHOL 5- LANETH 5: Ethoxylated lanolin alcohol HLB=7.5
- VOLPO S2: Polyethylene glycol-2, oleyl ether HLB=4.9
- VOLPO S10: Polyethylene glycol-10, oleyl ether HLB=12.4
- VOLPO S 20: Polyethylene glycol-20, oleyl ether HLB=15.3

EMPLEX

- Sodium stearyl-2-laclylate

HENKEL Inc.

- AVIROL: sodium tredecyl sulfate
- STANDAPOL I 30 E
- STANDAPOL T: TEA lauryl sulfate
- STANDAMID: cocamide DEA

HERCULES

- RETEN 763

HETERENE CHEMICAL Corp., Inc.

- HETOXAMATE ISO DSA PEG-ISO Disterate

HOECHST

- GENAMINOX
- HOSTAPURS AS 060

HUMKA PRODUCT

- KEMAMINE D-190 and P 190: Fatty nitrogen derivates

I.C.I.

- ARLACEL xxx:

  ARLACEL 20: HLB 8.6

  ARLACEL 80: Sorbitan monooleate HLB=4.3

  ARLACEL 83: Sorbitan sesquioleate HLB=4.3

  ARLACEL 186: Glycerol monooleate and propylene glycol mixture

- SPA xx:

  SPA 20: sorbitan monooleate HLB=8.6

  SPA 85: sorbitan trioleate HLB=3.7

- BRIJ xx:

  BRIJ 56: polyoxyethylene (10) cethyl ether

  BRIJ 58: polyoxyethylene (20) cethyl ether

  BRIJ 76: polyoxyethylene (10) stearyl ether

  BRIJ 96: polyoxyethylene (10) oleyl ether

BRIJ 98: polyoxyethylene (20) oleyl ether

BRIJ 721: polyoxyethylene (21) stearyl ether

- MYRJ 52: polyoxyl (40) stearate

KARLSHAMNS

- CAPTEX 810 A
- CAPMUL
  - CAPMUL POE-O
  - CAPMUL POE-S
  - CAPMUL POL-L
  - CAPMUL MCM
  - CAPMUL O
  - CAPMUL EMG-K
  - CAPMUL GMS 50
- CAPROL
  - CAPROL 10 G 2-0
  - CAPROL 10 G 10-0
  - CAPROL 6 G 2-0
  - CAPROL 6 G 2 S
  - CAPROL 3GS
  - CAPROL 3 G 0
  - CAPROL 100 4 G
  - CAPROL PGE 4 G
- Triglycerol
- Decaglycerol
- Hexaglycerol

LONZA

- Lonzest PEG 4 0
- Glycosperse 0-20
- Barlox 14: mixture of:

  N,N-dimethyl-1 dodecamine N oxide

  N,N-dimethyl-1 tetradecamine N oxide

  N,N-dimethyl-1 hexadecamine N oxide
- Barquat CME 35: N,N-cethyl ethyl morpholinium
- Glycomol 0: Sorbitan monooleate hexadecylalcohol

MONA INDUSTRIES

- Monoamid 71G, ADD and 150 ADD

PVO RESEARCH

- DREWPOL 10-4-0: decaglycerol tetraoleate
- DREWPOL 10-8-0: decaglycerol octaoleate
- DREWPOL 10-4-0: decaglycerol decaoleate

RHONE-POULENC

- IGEPAL CO xxx: Alkyl phenol-j-$(OCH_2CH_2)_nOH$

CO 210	HLB=4.8
CO 420	HLB=8.0
CO 530	HLB=10.0
CO 610	HLB=12.2
CO 630	HLB=13.0
CO 660	HLB=13.2
CO 710	HLB= 13.6
CO 730	HLB= 15.0

CO 850 HLB= 16.0

- IGEPAL CA xxx: Octyl phenol-j-$(OCH_2CH_2)_nOH$

CA 630 HLB=13.0

CA 720 HLB=14.6

CA 890 HLB=18.0

- IGEPAL DM 730: Dinonyl phenol-j-$(OCH_2CH_2)_nOH$ HLB=15.0

- GAFQUAT 755N and 755

- GANTREZ AN 149

- IGEPON TC 42: Polyethyleneoxy derivate

- PLASDOME K29-32: Polyvinylpyrrolidone (PVP)

- EMULPHOGENE BC 420: polyoxyethylated (3) tridecyl alcohol (HLB=8.0)

RHOM HAAS

- TRITON X15 and X114

SANDOZ

- Sandopan DTC

SIGMA

- Polyethylene sorbitan monooleate

- Polyethylene sorbitan trioleate

- Polyethylene sorbitan monosterate

SIPEX

- Sodium 2-ethylhexyl sulfate

STEPHAN

- AMMONYX SO: Hexaglycerol

- AMMONYX CO: Decaglycerol

- AMMONYX MO: Decaglycerol octaoleate

VAN DEN BERGH

- SANTONE 10-10-0, 3-1-S-X and 8-1-0

- PURFAX 60: Polysorbate 60

WITCO CORPORATION

- Emcol CC37 and 19

- WITCOLOATE A

DIVERS

- HAMPOXYL M30: Sodium myristoyl sarcosinate

- HAMPOXYL L30: Sodium lauroyl sarcosinate

- 2-Amino, 2-methyl propanol dodecyl sulphate

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