

**SYNTHESIS OF POLYMERIC CATIONIC SURFACTANT
FOR EMULSION POLYMERIZATION OF METHYL
METHACRYLATE AND VINYL ACETATE**

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JUNE 2008

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Date of submission : 5 May 2008

Date of defence examination : 10 June 2008

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JUNE 2008

**METİL METAKRİLAT VE VİNİL ASETATIN
EMÜLSİYON POLİMERİZASYONU İÇİN POLİMERİK
KATYONİK YÜZEY AKTİF MADDENİN SENTEZLENMESİ**

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Tezin Savunulduğu Tarih : 10 Haziran 2008**

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HAZİRAN 2008

ACKNOWLEDGEMENT

I would like to thank all the people who made this work possible. It is a pleasant aspect that I have now the opportunity to express my gratitude to all of them.

First of all, I am deeply indebted to my supervisor, Assoc. Prof. Dr. Bahire Filiz Şenkal, for her kind support and guidance.

This thesis is the result of two years' work whereby I have been accompanied and supported by many people. Special thanks to my teachers and lab-mates for all their help. Assoc. Prof. Dr. Yeşim Hepuzer, Assoc. Prof. Dr. Ayfer Sarac, Res. Assist. Erdem Yavuz, with all of you, it has really been a great pleasure.

I would also like to extend my gratitude to İpek Bilgili for the help given during the various stages of my thesis and my life.

I dedicate this thesis to my dear family for their patience, support and encouragement.

Thank you all...

May 2008

Murat YILDIRIM

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LIST OF ABBREVIATIONS

MMA	: Methyl Methacrylate
VAc	: Vinyl acetate
FT-IR	: Fourier Transform Infrared Spectroscopy
NMR	: Nuclear Magnetic Resonance Spectroscopy
UV-VIS	: Ultraviolet Visible Spectroscopy
M_n	: Number Average Molecular Weight
M_v	: Viscosity Average Molecular Weight
AIBN	: Azobisisobutyronitrile
HCl	: Hydrochloride
NaOH	: Sodium Hydroxide
APS	: Ammonium Persulfate
TEMED	: Tetramethylene ethylenediamine

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SYNTHESIS OF POLYMERIC CATIONIC SURFACTANT FOR EMULSION POLYMERIZATION OF METHYL METHACRYLATE AND VINYL ACETATE

SUMMARY

Conventional surfactants are typically characterized by a chemical structure that combines a hydrophilic group with one or two hydrophobic flexible alkyl chains of moderated length. In aqueous phase, small amounts of surfactant are enough to self-assemble into micellar microaggregates.

Surfactants are used in painting, emulsion polymerizations, adhesives, textile industry, etc. There are four different surface active materials. They are anionic, cationic, non-ionic and zwitterionic.

In this study, a new cationic polymeric surfactant has been synthesized with the reaction between Tetramethylene ethylenediamine (TEMED) and Dibromohexane.

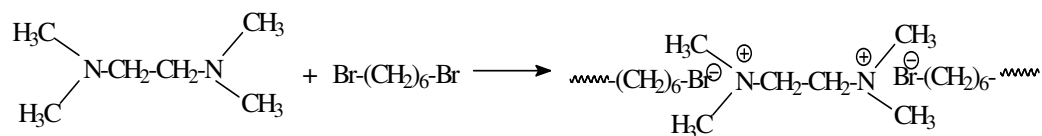


Figure 1. Schematic illustration of reaction between TEMED and Dibromohexane

This material has been characterized by FT-IR spectra and critical micelle concentration by using conductometric method.

The characterization of the polymeric surfactant was performed by using FT-IR spectroscopy. The FT-IR spectrum of cationic emulsifier (Figure 2) was as expected, with bands for the alkyl group at 2900–2800 cm^{-1} . If FT-IR spectrum of surfactant was compared with TEMED (Spectral Database for Organic Compounds, SDBS No: 2373) new bands were observed at 1133 cm^{-1} and 3010 cm^{-1} because of quaternization

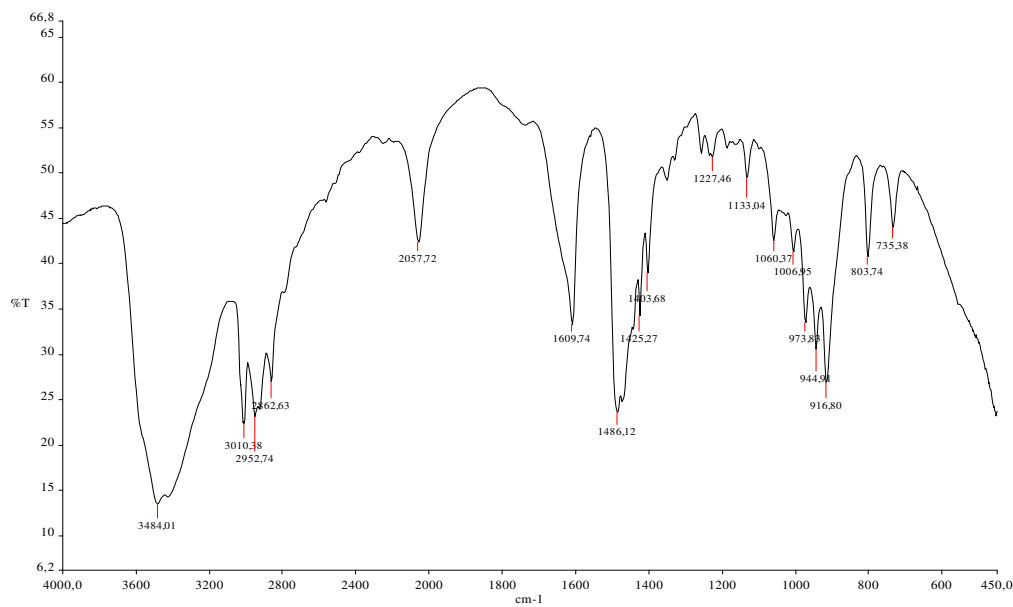


Figure 2. The FT-IR spectrum of the polymeric surfactant

Critical micelle concentration of the water-soluble polymer was determined by conductometric measurements. This value was calculated as $1,67 \times 10^{-2}$ g/ml (Figure 3).

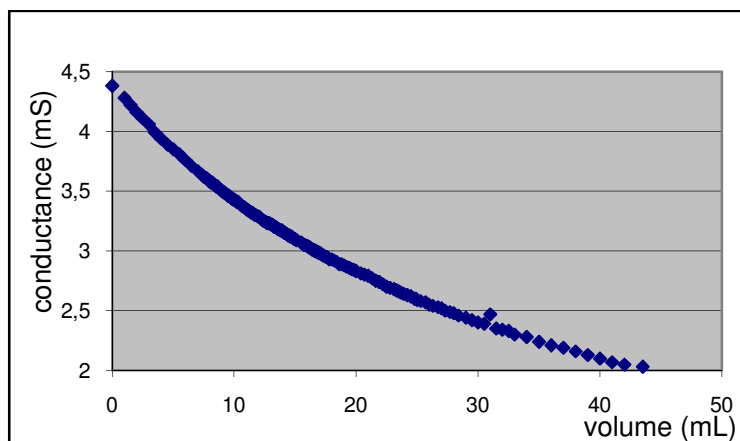


Figure 3. The CMC graph of the polymeric surfactant.

This material has been used for emulsion polymerization of Vinyl acetate (VAc) and Methyl methacrylate (MMA).

Polymerization reactions were performed by using different surfactant concentration and initiator concentrations. The polymerizations were performed at 70°C for Vinyl acetate and at 85°C for Methyl methacrylate in different time depending on the surfactant quantity. Obtained polymers were precipitated by adding NaCl and

polymers were filtered and washed with excess of hot water and methanol. The polymers were dried under vacuum at room temperature for 24 h.

Also, obtained polymers has been characterized by using surface tension and reometric measurements.

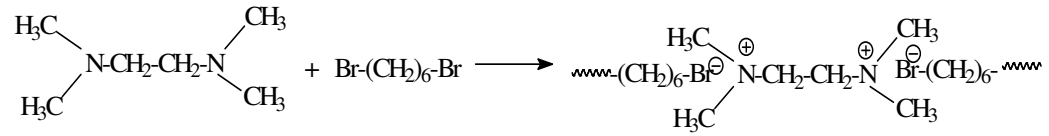
METİL METAKRİLAT VE VİNİL ASETATIN EMÜLSİYON POLİMERİZASYONU İÇİN POLİMERİK KATYONİK YÜZEY AKTİF MADDENİN SENTEZLENMESİ

ÖZET

Bilinen yüzey aktif maddeler genel olarak bir hidrofilik grubu, bir yada iki hidrofobik ve elastik alkil grupları ile birleştiren kimyasal yapılarına göre karakterize edilirler. Su fazı içerisinde misellerin kendiliğinden oluşması için az miktardaki yüzey aktif madde yeterli olmaktadır.

Yüzey aktif maddeler endüstriyel açıdan çok önemlidirler. Boya sektöründe, emülsiyon polimerizasyonlarında, yapıştırıcı ve tekstil gibi bir çok endüstride yüzey aktifler kullanılmaktadır. Anyonik, katyonik, non-iyonik ve amfoterik olmak üzere 4 çeşit yüzey aktif mevcuttur.

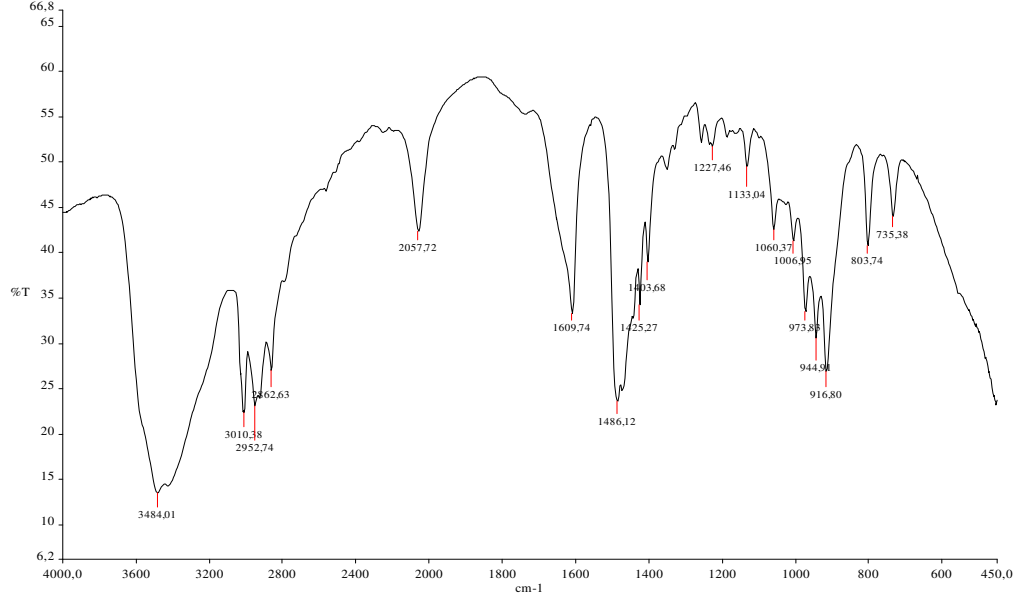
Bu çalışmamızda, yeni bir polimerik katyonik yüzey aktif madde Tetrametil etilendiamin (TEMED) ve Dibromoheksanın reaksiyonu ile sentezlenmiştir.



Şekil 1. TEMED ve Dibromoheksan arasındaki reaksiyonun şematik gösterimi

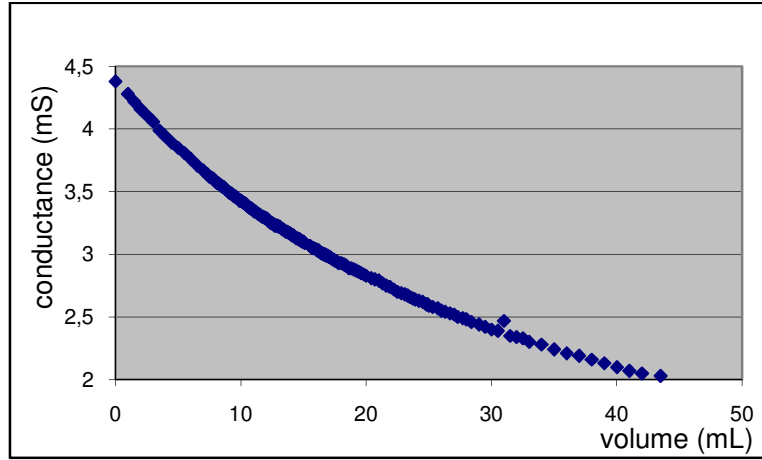
Sentezlenen bu madde FT-IR spektrumu ve kondüktometrik metot kullanılarak elde edilen kritik misel konsantrasyonu ile karakterize edilmiştir.

Katyonik yüzey aktif maddenin FT-IR spektrumu Şekil 2' de gösterilmiştir. 2900 - 2800 cm^{-1} arasında alkil grubu pikleri görülmektedir. Bu spektrum literatürde bulunan TEMED' e ait piklerle karşılaştırılmıştır ve kuaternizasyon nedeni ile 1133 cm^{-1} ve 3010 cm^{-1} değerlerinde yeni piklerin oluştuğu gözlemlenmiştir.



Şekil 2. Polimerik yüzey aktif maddenin FT-IR spektrumu

Suda çözünebilir polimerik katyonik yüzey aktif maddenin kritik misel konsantrasyonu kondüktometrik ölçüm ile hesaplanmıştır ve Şekil 3 kullanılarak bu değer $1,67 \times 10^{-2}$ g/mL olarak bulunmuştur.



Şekil 3. Polimerik yüzey aktif maddeye ait kritik misel konsantrasyonu grafiği

Elde edilen bu yüzey aktif Metil metakrilat (MMA) ve Vinil asetat (VAc)'in emülsiyon polimerizasyonunda kullanılmıştır.

Polimerizasyon reaksiyonları, farklı yüzey aktif ve başlatıcı konsantrasyonlarında gerçekleştirilmiştir. Polimerizasyon reaksiyonları MMA için 85°C, VAc için 70°C de yapılmıştır. Elde edilen polimerler daha sonra NaCl eklenerek çöktürülmüş,

filtrelenmiş ve sıcak su ve metanol kullanılarak yıkanmıştır. Polimerler daha sonra vakum içerisinde, oda sıcaklığında 24 saat boyunca kurutulmuştur.

Ayrıca, elde edilen polimerler yüzey gerilimi ve reometrik ölçümlerle de karakterize edilmişlerdir.

1. INTRODUCTION

A surfactant is a substance which stabilizes an emulsion, frequently an emulsifier (also known as an emulgent). Examples of food emulsifiers are egg yolk (where the main emulsifying chemical is lecithin), Honey and mustard, where a variety of chemicals in the mucilage surrounding the seed hull act as emulsifiers; proteins and low-molecular weight emulsifiers are common as well. In some cases, particles can stabilize emulsions as well through a mechanism called Pickering stabilization. Both mayonnaise and hollandaise sauce are oil-in-water emulsions that are stabilized with egg yolk lecithin. Detergents are another class of surfactant, and will chemically interact with both oil and water, thus stabilizing the interface between oil or water droplets in suspension. This principle is exploited in soap to remove grease for the purpose of cleaning. A wide variety of emulsifiers are used in pharmacy to prepare emulsions such as creams and lotions.

Quaternary ammonium cations, also known as quats, are positively charged polyatomic ions of the structure NR_4^+ with R being alkyl groups. Unlike the ammonium ion NH_4^+ itself and primary, secondary, or tertiary ammonium cations, the quaternary ammonium cations are permanently charged, independent of the pH of their solution. Quaternary ammonium cations are synthesized by complete alkylation of ammonia or other amines.

Quaternary ammonium salts or quaternary ammonium compounds (called quaternary amines in oilfield parlance) are salts of quaternary ammonium cations with an anion. They are used as disinfectants, surfactants, fabric softeners, and as antistatic agents (e.g. in shampoo). In liquid fabric softeners, the chloride salts are often used. In dryer anticling strips, the sulfate salts are often used. This is also a common ingredient in many spermicidal jellies.

Surfactants can be categorized according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution):

- Anionic surfactants; where the head group of the molecule has a negative charge,
- Nonionic surfactants; where the head group has no ionic character,
- Cationic surfactants; where the head group bears a positive charge,
- Ampholytic surfactants; where both positive and negative charges are present.

Cationic surfactants, which are most relevant to the present study, usually fall into one of the following categories: long-chain amines or polyamines and their respective salts, quaternary ammonium salts (e.g. hexadecyltrimethyl ammonium bromide), oligo (ethylene oxide) amines and their quaternized derivatives, and amine oxides. Cationic surfactants are used in many applications from fabric softeners and toiletries to adhesion promoters in asphalt and corrosion inhibitors.

In the present work a new polymeric cationic surfactant was synthesized. This material was used in the emulsion polymerization of Methyl methacrylate (MMA) and Vinyl acetate (VAc).

2. THEORETICAL PART

2.1 Surfactants

Surfactants and polymers are extensively used as excipients in drug delivery. However, although the understanding of the physicochemical properties and behavior of such compounds both in solution and at interfaces has undergone a dramatic development in the last couple of decades, the new findings are frequently not implemented to the full extent possible in various application areas.

Surfactants are low to moderate molecular weight compounds which contain one hydrophobic part, which is generally readily soluble in oil but sparingly soluble or insoluble in water, and one hydrophilic (or polar) part, which is sparingly soluble or insoluble in oil but readily soluble in water (Figure 2.1).

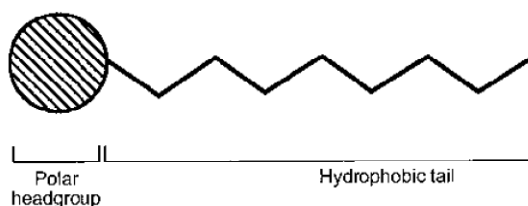


Figure 2.1. Schematic illustration of a surfactant molecule.

Due to this “schizophrenic” nature of surfactant molecules, these experience suboptimal conditions when dissolved molecularly in aqueous solution. If the hydrophobic segment is very large the surfactant will not be water-soluble, whereas for smaller hydrophobic moieties, the surfactant is soluble, but the contact between the hydrophobic block and the aqueous medium nevertheless energetically less favorable than the water-water contacts.

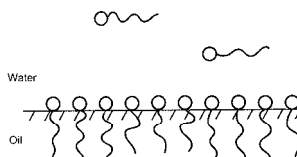


Figure 2.2. Schematic illustration of the adsorption of surfactants at the oil-water interface.

Alternatives to a molecular solution, where the contact between the hydrophobic group and the aqueous surrounding is reduced, therefore offer ways for these systems to reduce their free energy. Consequently, surfactants are surface active, and tend to accumulate at various interfaces, where the water contact is reduced (Figure 2.2).

Another way to reduce the oil-water contact is self-assembly, through which the hydrophobic domains of the surfactant molecules can associate to form various structures, which allow a reduced oil-water contact. Various such structures can be formed, including micelles, microemulsions, and a range of liquid crystalline phases (Figure 2.3).

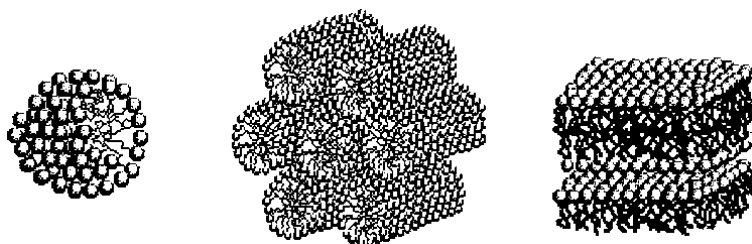


Figure 2.3 : Schematic illustration of some different self-assembled structures formed in surfactant systems.

The type of structures formed depends on a range of parameters, such as the size of the hydrophobic domain, the nature and size of the polar head group, temperature, salt concentration, pH, etc. Through varying these parameters, one structure may also turn into another, which offers interesting opportunities in triggered drug delivery.

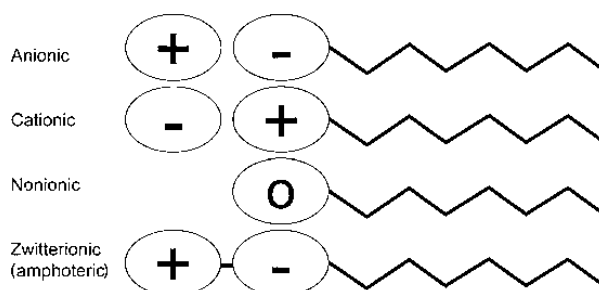


Figure 2.4. Schematic illustration of the various types of surfactants.

Surfactants are classified according to their polar headgroup; i.e., surfactants with a negatively charged headgroup are referred to as anionic surfactants, whereas cationic surfactants contain polar headgroups with a positive charge. Uncharged surfactants are generally referred to as nonionic, whereas zwitterionic surfactants contain both a negatively charged and a positively charged group (Figure 2.4).

Anionic surfactants (Figure 2.5) constitute the largest group of available surfactants. Examples of such surfactants include;

1. Fatty acid salts (“soaps”)
2. Sulfates
3. Ether sulfates
4. Phosphate esters

A common feature of all anionic surfactants is that their properties, e.g., surface activity and self-assembly, are quite sensitive to salt, and particularly divalent or multivalent cations. A commonly experienced illustration of this is poor solubility, foaming, and cleaning efficiency of alkyl sulfate surfactants in salt or hard water. Naturally, this salt dependence also offers opportunities in drug delivery. Sulfates are also somewhat sensitive toward hydrolysis, particularly at low pH.

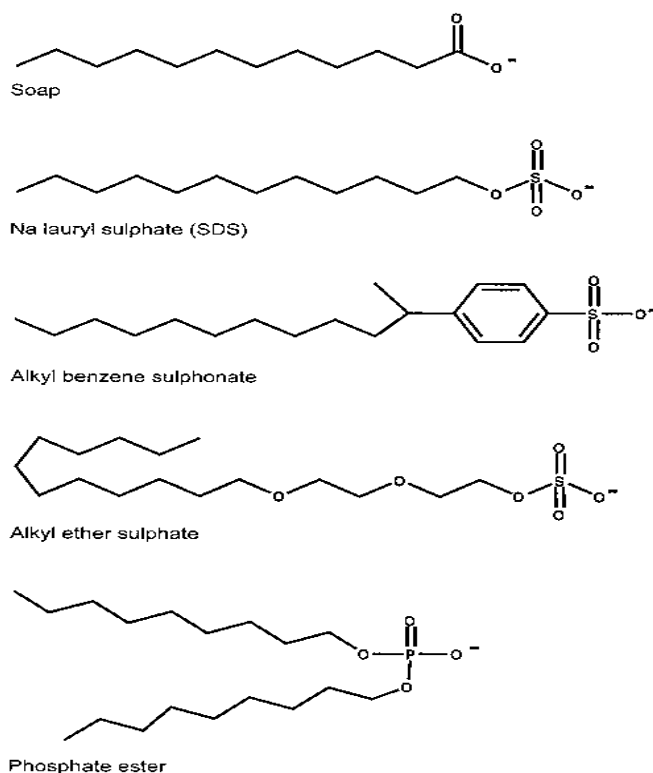


Figure 2.5. Chemical structure of some commonly used anionic surfactants. Cationic surfactants are frequently based on amine-containing polar headgroups (Figure 2.6).

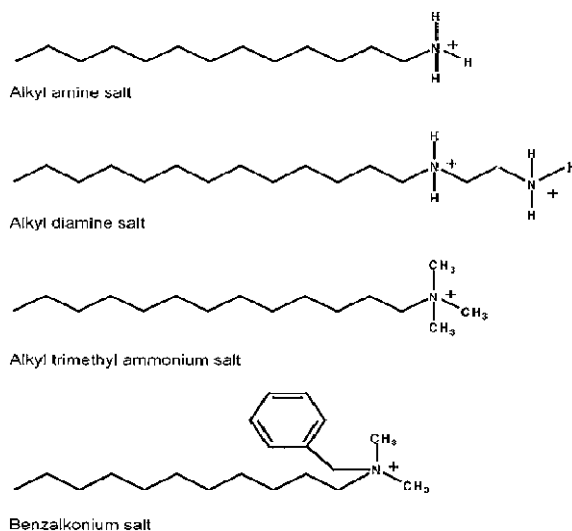


Figure 2.6. Chemical structure of some commonly used cationic surfactants.

Due to their charged nature, the properties of cationic surfactants, e.g., surface activity or structure formation, are generally strongly dependent on the salt concentration, and on the valency of anions present. Cationic surfactants are frequently used as antibacterial agents, which may be advantageous also in certain drug delivery applications, such as delivery systems to the oral cavity. However, cationic surfactants are frequently also irritant and some times even toxic.

Nonionic surfactants, i.e., surfactants with an uncharged polar headgroup, are probably the ones used most frequently in drug delivery applications, with the possible exception of phospholipids. In particular, nonionic surfactants used in this context are often based on oligo(ethylene oxide)-containing polar head groups (Figure 2.7).

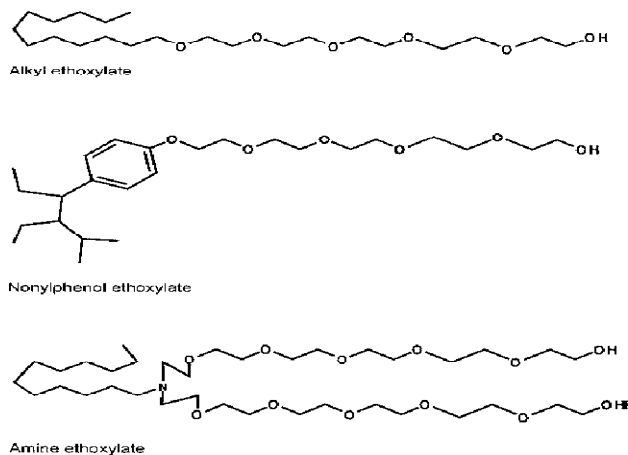


Figure 2.7. Chemical structure of some commonly used nonionic surfactants.

Due to the uncharged nature of the latter, these surfactants are less sensitive to salt, but instead quite sensitive to temperature, which may be used as a triggering parameter in drug delivery with these surfactants. The critical micellization concentration for such surfactants is generally much lower than that of the corresponding charged surfactants, and partly due to this, such surfactants are generally less irritant and better tolerated than the anionic and cationic surfactants.

Zwitterionic surfactants are less common than anionic, cationic, and nonionic ones. Frequently, the polar headgroup consists of a quaternary amine group and a sulfonic or carboxyl group (Figure 2.8).

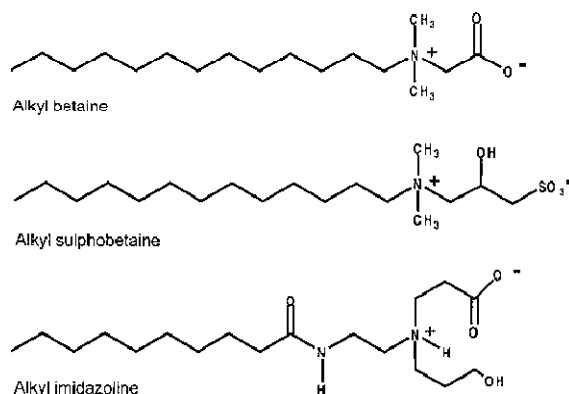


Figure 2.8. Chemical structure of some typical zwitterionic surfactants.

Due to the zwitterionic nature of the polar headgroup, the surfactant charge changes with pH, so that it is cationic at low pH and anionic at high pH. Due to the often low irritating properties of such surfactants, they are commonly used in personal care products.

2.2 Micelles

2.2.1 Structure and dynamics of micellar systems

A notable feature of surfactants is their ability to self-associate to form micelles (Figure 2.9). Since micelles consist of surfactant molecules packing in a spacefilling manner numerous parameters of the surfactant solution change at the critical micellization concentration (cmc). For example, since the micelles consist of many individual surfactant molecules, any parameter related to the size or diffusion in surfactant solutions can be used to detect the micellization, e.g., through scattering methods and nuclear magnetic resonance (NMR). Also, the micellar core contains little water (see below); hence solubilization of hydrophobic dyes is initiated at the

cmc, and fluorescence investigations with probes sensitive for the polarity of the environment can be used to detect micellization.

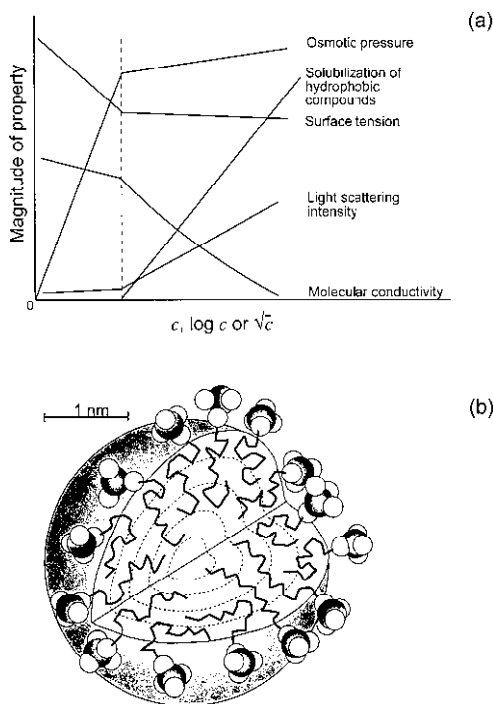


Figure 2.9. (a) Schematic illustration of how a range of experimentally accessible parameters change with the surfactant concentration and how this can be used to detect the cmc. (b) Schematic illustration of a spherical micelle.

Also, a range of other techniques, such as conductivity (ionic surfactants), osmotic pressure, and surface tension, may be used to determine the cmc. The main driving force for micelle formation in aqueous solution is the effective interaction between the hydrophobic parts of the surfactant molecules, whereas interactions opposing micellization may include electrostatic repulsive interactions between charged head groups of ionic surfactants, repulsive osmotic interactions between chainlike polar head groups such as oligo(ethylene oxide) chains, or steric interactions between bulky head groups.

Given the delicate balance between opposing forces, it is not surprising that surfactant self-assembly is affected by a range of factors, such as the size of the hydrophobic moiety, the nature of the polar head group, the nature of the counterion (charged surfactants), the salt concentration, pH, temperature, and presence of cosolutes. Probably the most universal of all these is the size of the hydrophobic domain(s) in the surfactant molecule. With increasing size of the hydrophobic domain, the hydrophobic interaction increases, thereby promoting micellization. As

an illustration of this, Figure 2.2 shows the chain length dependence of the cmc for some different surfactants. As can be seen, the cmc decreases strongly with an increasing number of carbon atoms in the alkyl chain, irrespective of the nature of the polar head group. As a general rule, the cmc decreases a factor of 2 for ionic surfactants and with a factor of 3 for nonionic surfactants on addition of one methylene group to a surfactant alkyl chain. The extent of the decrease also depends on the nature of the hydrophobic domain, in terms of both structure (e.g., single chain vs. double chain surfactants) and composition (e.g., fluorinated surfactants), but qualitatively, the same effect is observed for all surfactants.

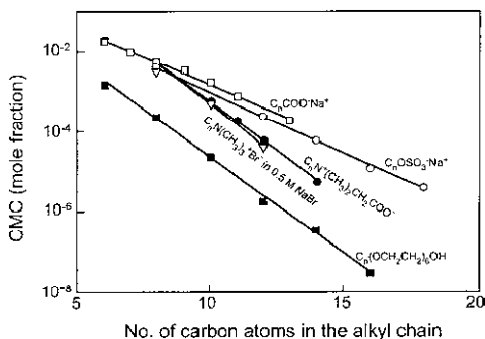


Figure 2.10. The dependence of the cmc with the length of the hydrophobic domain for a number of alkyl chain surfactants with different polar head group.

The dependence of the micellization on the nature of the polar head group is less straightforward than that of the alkyl chain length. Nevertheless, the cmc of nonionic surfactants is generally much lower than that of ionic ones, particularly at low salt concentrations, which is due to the repulsive electrostatic interaction between the charged head groups opposing micellization (Figure 2.10).

For nonionic surfactant of the oligo(ethylene oxide) type, an increasing number of ethylene oxide groups at a constant alkyl chain length results in an increasing cmc as a consequence of an increasing osmotic repulsion between the oligo(ethylene oxide) chains when these grow larger (Figure 2.11). The length of the oligo(ethylene oxide) chains affects also the packing of the surfactant molecules in the micelle. More precisely, with an increasing length of the oligo(ethylene oxide) chain, the head group repulsion increases, which tends to increase the curvature of the aggregates, and hence results in smaller and more spherical micelles. The latter effect can be observed, e.g., from the micellar size or aggregation number.

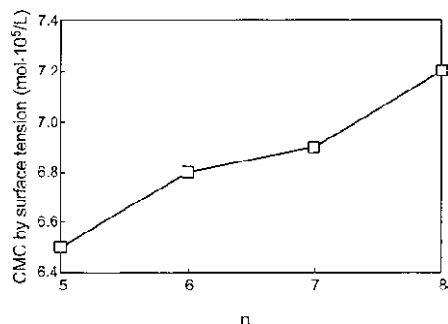


Figure 2.11. Effect of the length of the oligo(ethylene oxide) chain n on the cmc for a series of $C_{12}E_n$ surfactants.

Cosolutes in general tend to affect the micellization in surfactant systems. Examples of such cosolutes include oils (or other hydrophobic compounds), salt, alcohols, and hydrotropes. Of these, salt plays a particularly important role, particularly for ionic surfactants. Thus, on addition of salt, the electrostatic repulsion between the charged head group is screened. As a consequence, the repulsive interaction opposing micellization becomes relatively less important, and the attractive driving force for micellization therefore dominates to a larger extent. As a result of this, the cmc decreases on addition of salt (Figure 2.12).

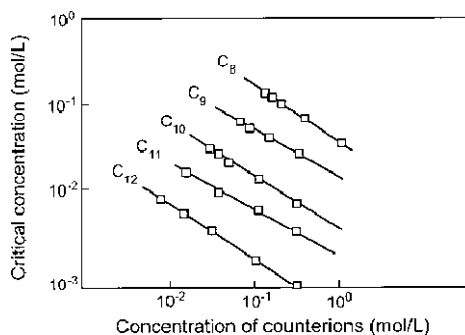


Figure 2.12. Effect of sodium chloride on the cmc of sodium alkyl sulfate surfactants.

For nonionic surfactants, on the other hand, addition of low or moderate concentrations of salt has little influence on the micellization due to the absence of charges in these systems. At very high salt concentrations (~ 0.1 – 1 M), so-called lyotropic salt effects are typically observed. Depending on the nature of both the cation and the anion of the salt, the presence of the salt may either promote or preclude micellization.

For ionic surfactants, the presence of salt also affects the micellar size and aggregation number. In particular, screening of the repulsive electrostatic interaction

through addition of salt facilitates a closer packing of the surfactant head groups, and therefore results in a micellar growth (Figure 2.13).

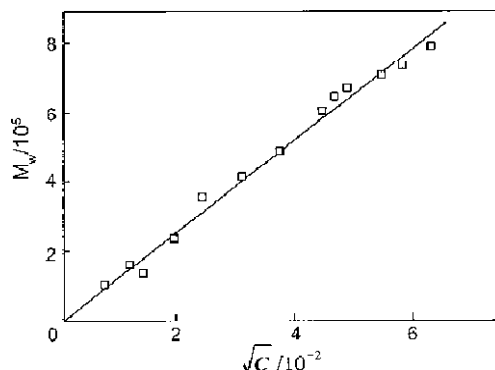


Figure 2.13. Effect of added salt on the micellar aggregation number for CTAB.

Again, for nonionic surfactants, little or no such dependence is observed. Instead, many nonionic surfactants, notably those containing oligo(ethylene oxide) groups, display a sensitivity regarding temperature. With increasing temperature, surfactants and polymers containing oligo(ethylene oxide) or its derivatives display a decreased water solubility. At sufficiently high temperature, usually referred to as the lower consolute temperature (LCT) or the cloud point (CP), such molecules phase separate to form one dilute and one more concentrated phase. Note that this behavior is opposite to what is observed for most other types of surfactants and polymers, which display increasing solubility/miscibility with increasing temperature.

The decreased solvency for the oligo(ethylene oxide) moieties with increasing temperature results in a decreased repulsion between the polar head groups in ethylene oxide-based surfactants, and hence micellization is favored at higher temperature. Consequently, the cmc displayed by these surfactants decreases with increasing temperature (Figure 2.14).

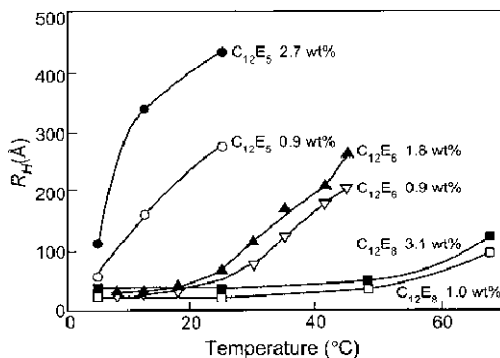


Figure 2.14. Effect of temperature on the micellar size RH for $C_{12}E_n$ surfactants.

For ionic surfactants, but also for nonionic surfactants other than those based on oligo(ethylene oxide), the general rule is that the temperature dependence of the micellization and the structure of the micelles formed is rather minor. Organic cosolutes in general play an important role in technical systems containing surfactants. This is the case not the least in drug delivery, where surfactants are used in order to facilitate the efficient and safe administration of a drug. The effect of a cosolute on the micellization in surfactant systems to a large extent depends on the nature of the cosolute. As illustrated above, salts have large effects on the micellization in ionic surfactant systems, but rather weak effects in nonionic surfactant systems. For uncharged cosolutes, the effect on the micellization in surfactant systems depends both on the nature of the cosolute and that of the surfactant, and both an increase and decrease of the cmc on addition of the cosolute is possible.

Of particular interest for the use of micellar systems in drug delivery are hydrophobic solutes, which are essentially insoluble in water but readily soluble in oil and therefore also in the hydrophobic core of micelles. As indicated above, the amount of a hydrophobic solute solubilized by a surfactant solution below the cmc is very limited. Above the cmc, on the other hand, the hydrophobic substance is solubilized in the micelles (Figure 2.15). Indeed, the capacity of surfactant systems to solubilize hydrophobic substances constitutes one of the single most important properties of such systems, as this forms the basis for the use of surfactants in numerous industrial contexts.

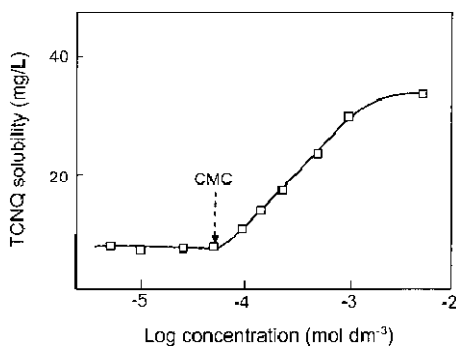


Figure 2.15. Solubility of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in aqueous solution of $C_{12}E_8$ at 25°C.

From simple space-filling considerations it is evident that the solubilization of a hydrophobic solute in the core of the micelles causes the latter to grow. At the same time, hydrophobic solutes may promote micellization and cause a decrease in the cmc. This is not entirely unexpected, since reducing the cmc in order to accommodate

the oil in a one-phase system may offer an opportunity for free energy minimization for the system as a whole.

Finally, it is important to note that surfactant micelles are not static structures, but rather that the schematic illustration shown in Figure 2.9 represents an instant “snapshot” of such a structure.

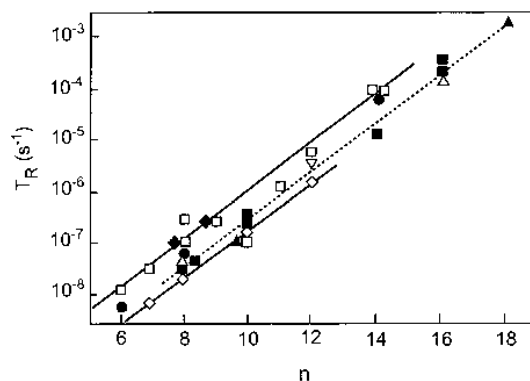


Figure 2.16. Effects of the alkyl chain length n of alkyl-based surfactants on heaverage residence time TR for a surfactant molecule in a given micelle. Open squares: sodium alkylsulfates; filled diamonds: sodium alkylsulfonates; filled squares: sodium alkylcarboxylates; open diamonds: potassium alkylcarboxylates; open square: cesium decylcarboxylate; filled circles: alkylammonium chlorides; filled triangles: alkyltrimethylamine bromides; open triangles: alkylpyridinium chlorides; filled squares: alkylpyridinium bromides; reversed open triangle: dodecylpyridinium iodine.

Thus, micelles are highly dynamic structures, where the molecules remain essentially in a liquid state. Also, the individual surfactant molecules are freely exchanged between micelles and between micelles and the aqueous solution. The residence time for the surfactant molecules in one given micelle is generally very short, but increasing about one order of magnitude for each ethylene group added to the surfactant hydrophobic tail (Figure 2.16).

2.2.2 Block copolymer micelles

Closely related to low molecular weight surfactants in many ways concerning self-assembly are block copolymers. This is particularly true for simpler block copolymer systems, such as diblock and triblock copolymers, which form not only micelles in dilute aqueous solution but also a range of liquid crystalline phases and microemulsions with oil and water. Such “polymeric surfactants” have found widespread use, not the least in drug delivery, as will be discussed in some detail below.

Although there has been extensive work on a range of block copolymer systems, much of this work has concerned solvent-based systems. During the last decade, however, a number of water-soluble block copolymer systems have been investigated concerning their physicochemical behavior, e.g., regarding self-association. In particular, much of the work has involved PEO-based copolymers [PEO being poly(ethylene oxide)], and these are also the ones of largest interest in the present context. A number of hydrophobic blocks have been investigated for PEO-based block copolymers, including poly(propylene oxide), poly(styrene), alkyl groups, poly(butylene oxide), poly(lactide), and poly(caprolactone). In particular, interest has focused on PEO/PPO block copolymers (PPO being polypropylene oxide), mainly due to their commercial accessibility in a range of compositions and molecular weights. Composition and molecular weight are two of the prime parameters of interest for block copolymer systems. In analogy to low molecular weight nonionic surfactants, micellization is promoted by an increasing length of the hydrophobic block(s) and decreasing length of the hydrophilic one(s) (Figure 2.17). From the slope of the decrease in the cmc and in the micellar aggregation number with an increasing number of hydrophobic groups, the hydrophobicity of the hydrophobic groups may be estimated. Such an analysis yields “hydrophobicity ratios” for propylene oxide (P), lactide (L), caprolactone (C), butylene oxide (B), and styrene (S) of 1:4:5:6:12.

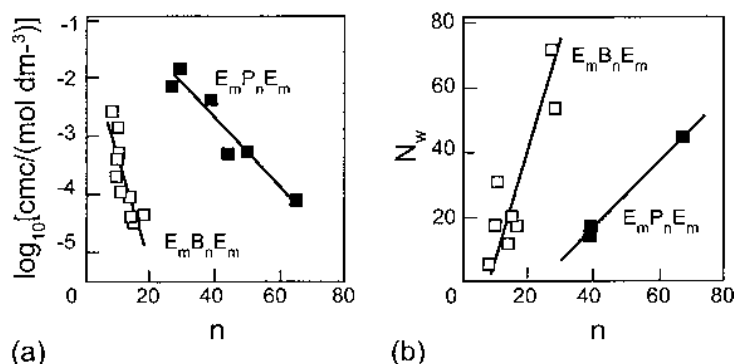


Figure 2.17. Effect of the length of the hydrophobic block n on the cmc (a) and micellar aggregation number N_w (b) of $E_m B_n E_m$ and $E_m P_n E_m$ triblock copolymers.

Also, the molecular architecture affects micellization in block copolymer systems. As can be seen in Figure 2.18, diblock ($E_m B_n$) copolymers self-associated more readily than triblock ($B_n/2E_m B_n/2$ and $E_m/2B_n E_m/2$) copolymers of the same total molecular weight and composition. The origin of this is that less efficient packing is achieved with the triblock copolymers, in the case of the BAB copolymer due to the

hydrophilic block being a loop rather than a tail, and in the ABA case due to the presence of two rather than one hydrophilic tail.

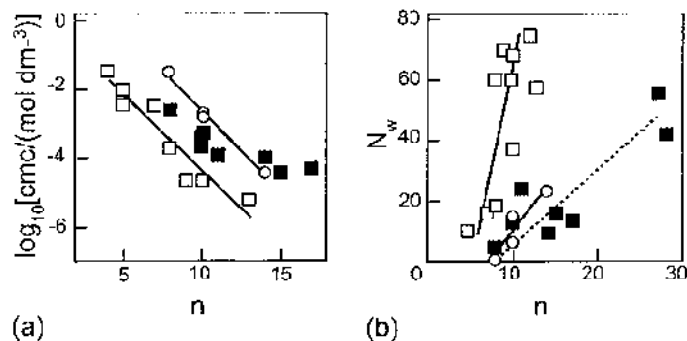


Figure 2.18. Effect of the number of butylene oxide groups n on the cmc (a) and micellar aggregation number N_w (b) for E_mB_n (open squares), $B_n/2E_mB_n/2$ (circles), and $E_n/2B_nE_n/2$ (filled squares) copolymers.

The micellization of PEO-containing block copolymers is promoted by increasing temperature. As with the low molecular weight surfactants, this is due to a decreased solvency of the PEO domain(s). However, for PEO/PPO copolymers, the decreased aqueous solubility of the PPO domain(s) with increasing temperature also contributes to this behavior. Quantitatively, the temperature dependence of the cmc is quite strong for many PEO/PPO block copolymers. The concentration-induced aggregation at a fixed temperature, on the other hand, is frequently quite gradual, and the determination of the cmc in the traditional manner therefore difficult. The cmc values so determined frequently span widely, e.g., between different experimental methods used, but also display batch-to-batch variations. Therefore, the onset of self-assembly in such systems is often identified by a critical micellization temperature at a fixed polymer concentration (cmt), rather than by a cmc at fixed temperature (Figure 2.19).

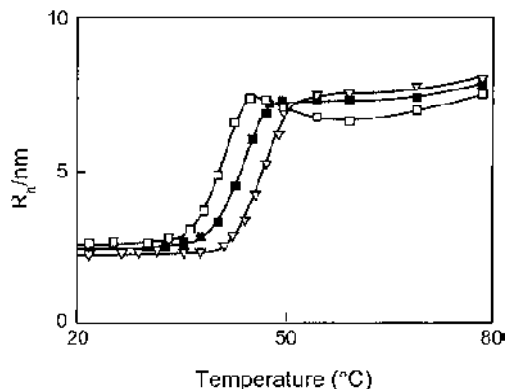


Figure 2.19. Temperature-dependent hydrodynamic radius R_h of Pluronic F68 at a bulk concentration of 51.7 (open squares), 25.0 (filled squares), and 12.5 (open triangles) $\text{mg}\cdot\text{ml}^{-1}$.

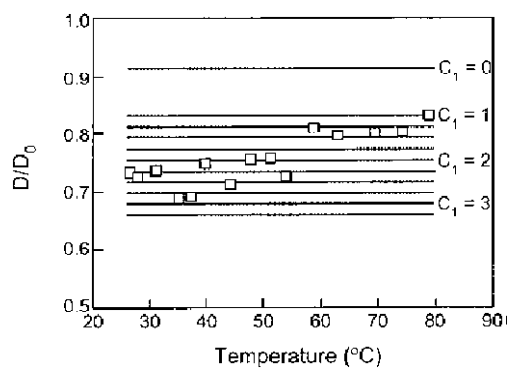


Figure 2.20. Effects of temperature on the number of water molecules bound per monomer C_1 in Pluronic F127 micelles, determined from the water self-diffusion (D/D_0).

There is also micellar growth with increasing temperature. However, in the general case, the increase in the micellar aggregation number is significantly stronger than that in the micellar radius, which indicates that the block copolymers pack more efficiently with increasing temperature. As with the E_0 containing low molecular weight surfactants, this is an effect of the decreasing solvency of the polymer with increasing temperature. This also means that the hydration of the polymer molecules decreases with increasing temperature (Figure 2.20).

The effects of cosolutes on the self-assembly of PEO/PPO block copolymers are quite similar to those on low molecular weight PEO-containing surfactants. Thus, effects of salts on the micellization in these block copolymer systems are minor at low to medium salt concentration, whereas at high salt concentration ($\sim 0.1 - 1$ M), lyotropic salt effects are observed. Furthermore, hydrophobic solutes may induce micellization. An illustration of this is given in Figure 2.21.

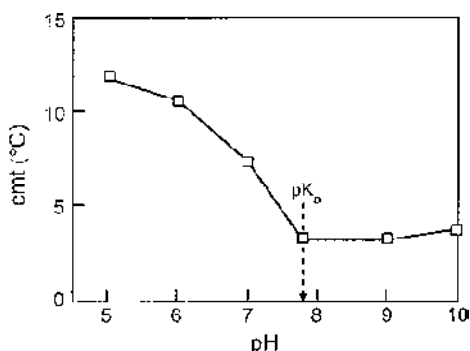


Figure 2.21. cmt as a function of pH from a formulation containing 5 wt% of active ingredient (50/50 mol/mol of lidocaine and prilocaine), 15.5 wt% Lutrol F127, and 5.5 wt% Lutrol F68.

As can be seen, the presence of lidocaine/prilocaine has little effect on the cmc for this copolymer system at $\text{pH} \leq \text{pKa}$ (7.86 and 7.89 for lidocaine and prilocaine,

respectively), i.e., where these compounds are fully ionized and readily soluble in water, and therefore behaving as ordinary salt. On increasing pH, on the other hand, lidocaine and prilocaine become less soluble in water as a result of deprotonation, and at $\text{pH} \geq \text{pKa}$ behave essentially as sparingly soluble oils, thus promoting micellization and lowering cmt. The localization of the solubilized molecule depends on the properties of the solubilize, notably its hydrophobicity. The more hydrophobic the solubilize, the more it tends to be localized in the core of the micelles. More amphiphilic molecules, on the other hand, tend to be located preferentially in the micellar interfacial layer.

An interesting difference between alkyl-based surfactants, on one hand, and PEO/PPO block copolymer, on the other, is that the hydrophobic moiety is significantly more polar in the latter case. This means that there is intermixing between the PEO and PPO blocks, but also that there is a significant amount of water present also in the core of the micelles formed by PEO/PPO block copolymers (Figure 2.22). With increasing temperature, however, there is a decreased hydration of the polymer.

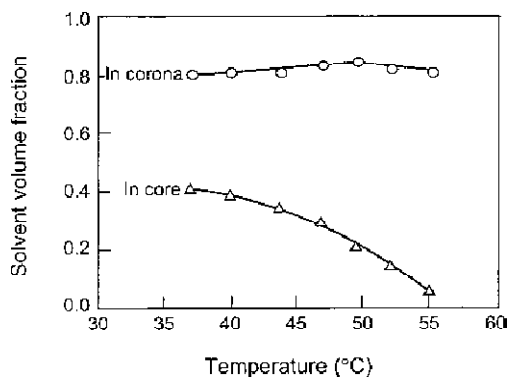


Figure 2.22. Volume fraction of water in the micellar core (triangles) and corona (circles) for a 2.5 wt% Pluronic L64 in D_2O .

Due to the partial polarity of the PPO block and the presence of water also in the micellar core, the solubilization capacity of PEO/PPO block copolymers differs somewhat from that of alkyl-based low molecular weight surfactants, where the water penetration to the micellar core is negligible. More specifically, while the solubilization of aromatic hydrocarbons may be significant in micelles formed by PEO/PPO block copolymers, that of aliphatic hydrocarbons is more limited. The amount solubilized also depends on the molecular volume of the solubilize, and the larger the solubilized molecule, the lower the solubilization (Figure 2.23). Also, the structure of the copolymer affects the solubilization, and the solubilization capacity increases with an increasing molecular weight and an increasing PPO content of the block copolymer (Figure 2.24).

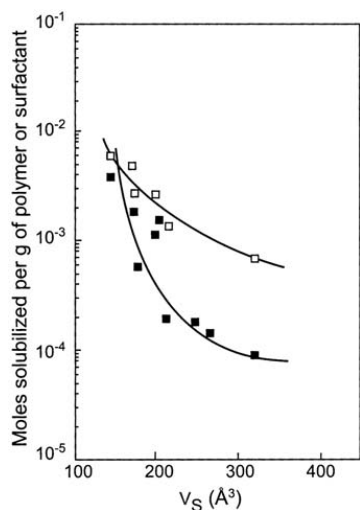


Figure 2.23. Effect of the molecular volume V_S on the extent of solubilization of hydrocarbons in SDS (open symbols) and Pluronic F127 (filled symbols) micelles.

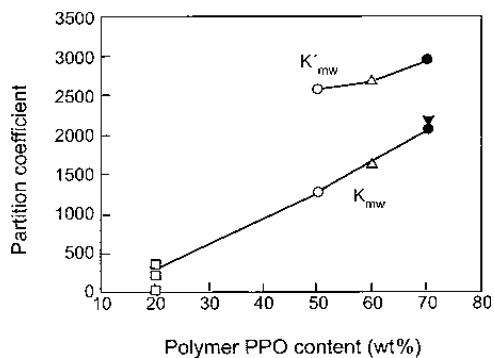


Figure 2.24. Relation between the micelle-water partition coefficient K_{mw} for naphthalene in PEO/PPO block copolymer micelles and the PPO content of the block copolymer. Shown also is K'_{mw} , the partition coefficient normalized with the polymer PPO content.

As with micelle formation as such, the solubilizing capacity of block copolymers also depends on the molecular architecture, with a lower degree of solubilization in tetrabranched PEO/PPO copolymers (Tetronics) than in PEO-PPO-PEO copolymers (Pluronics). There are several reasons for the observed dependence of the polymer molecular weight, composition, and architecture on its solubilizing capacity, all relating to the micelle formation and structure. For solubilization to be efficient, the micelles formed should preferably be of a sufficiently high aggregation number and contain a sufficiently large and hydrophobic micellar core. Since micellization is promoted by an increasing PPO content and precluded by branching of the copolymer, the solubilization is improved with an increased PPO content, and is poorer for tetrabranched than for linear block copolymers.

As long as spherical micelles are formed, higher molecular weight block copolymers form larger micelles than low molecular weight ones, and are therefore expected to be more efficient solubilizers. However, spherical micelles are not always formed, and both the aggregation number and the shape of the micelles may change on solubilization, which affect the latter. As a general rule, however, larger micelles are more efficient solubilizers than small ones. For PEO/PPO block copolymers, where the block segregation is incomplete, and where also the micellar core contains some water, increasing the molecular weight also has another effect, in that the segregation between the blocks increases with the polymer molecular weight. This, in turn, results in a decreased polarity of the micellar core, thereby facilitating solubilization.

A striking difference between low molecular weight surfactants and many (unfractionated) block copolymers is that while the former are usually well defined and reasonably homogeneous and monodisperse, the latter frequently contain a range of molecular weights and compositions. Since fractions containing different molecular weights and compositions display different self-assembly, the overall micellization process for such systems is gradual. Furthermore, the composition of the micelles changes during this process, e.g., with an increasing polymer concentration. Thus, in the early stages of micellization, the micelles are dominated by the fractions which have the highest tendency to self-assemble (e.g., those with the highest content of the hydrophobic block, or diblock impurities in the case of triblock copolymers), whereas at higher total polymer concentration, the micellar composition approaches that of the overall average of the system. From an experimental point of view, this gradual transition makes the micellization more difficult to investigate for technical block copolymer (and surfactant) systems, and the cmc loses its strict meaning. Most likely, this has contributed to the rather widely differing cmc values reported for commercial block copolymers (e.g., the Pluronics) over the years.

Another difference between low molecular weight surfactants and block copolymers concerns the dynamics in micellar systems. As discussed above, the average residence time for surfactant molecules in micelles increases strongly with the number of methylene group in the hydrophobic tail(s). Due to the very large hydrophobic group(s) frequently present in block copolymers, block copolymer micelles are characterized by much slower kinetics than those formed by low molecular weight surfactants. For example, high molecular weight Pluronic copolymers display an exceedingly slow micellar dynamics. Thus, micelles can, at

least in certain cases, be separated from the unmicellized molecules in size exclusion chromatography experiments typically spanning over more than an hour. This is an astonishing result since it shows that the micelles do not disintegrate over the time of the experiment despite the free polymer concentration surrounding the micelles being below cmc. In fact, the possibility of separating micelles from unmicellized polymers for at least some block copolymer systems offers a way to follow the micellization process, and to determine the cmt (Figure 2.25).

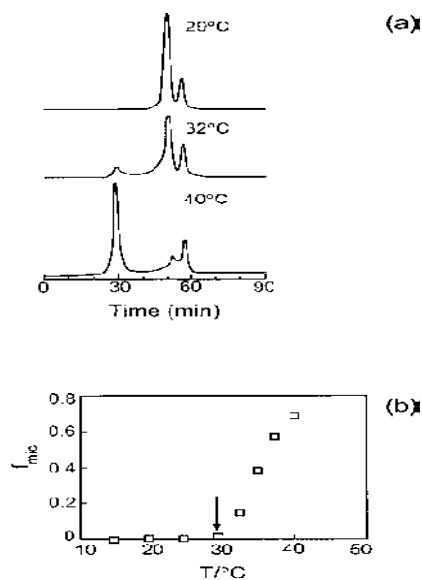


Figure 2.25 (a) Size exclusion chromatography trace for an aqueous Pluronic F127 solution at different temperatures. The peak appearing at an elution time of 30 min corresponds to micelles, whereas the peaks at 50–60 min correspond to the nonmicellized polymers (with impurities). (b) Temperature dependence of the relative intensity of the peak corresponding to micelles f_{mic} . The arrow indicates the cmt.

From a practical drug delivery perspective, this slow disintegration kinetics offers some possibilities. For example, while micelles formed by low molecular weight surfactants disintegrate rapidly after parenteral administration of a surfactant solution unless the surfactant concentration is very high, drug-loaded block copolymer micelles may be administered in a similar way without disintegrating over an appreciable time period. Without any doubt, the slow disintegration kinetics of the micelles formed by at least some block copolymers has contributed significantly to their successful use in drug delivery. Although the vast majority of the work performed on block copolymer micelles in both basic studies and drug delivery work has been performed with PEO/PPO block copolymers, there is a current development to find new block copolymers for such uses. Over the last few years in

particular, this has involved the development of biodegradable hydrophobic blocks, such as poly(lactide), poly(caprolactone), poly(β -benzyl-L-aspartate), poly(γ -benzyl-L-glutamate), poly(aspartic acid), and poly(L-lysine). Such systems offer possibilities in drug delivery in that the degradation allows control of the drug release rate and other drug formulation performances, and the elimination of the polymer from the body is facilitated.

2.2.3 Characterization of micellar systems

There are a number of aspects of surfactant and block copolymer micelles which are interesting to characterize in order to learn more about a particular system. The main one of these is without doubt the onset of micellization, i.e., the cmc or cmt. Once this has been determined, one may proceed to determine the size of the micelles formed, and the micellar aggregation number. In some cases, it may also be interesting to investigate other parameters, such as the shape of the micelles, the state of hydration, microviscosity in the micellar core, and the micellar dynamics. As indicated above, there are numerous methods to determine the cmc or the cmt, including surface tension measurements, scattering experiments, NMR, fluorescence spectroscopy, calorimetry, osmotometry, conductivity, and solubilization experiments (Figure 2.9). Of these, three are discussed here, i.e., surface tension because this is the most frequently used method for cmc determinations, and scattering and NMR techniques because these are very versatile, and may provide information also about other aspects of micellar systems, such as the micellar size, the micellar aggregation number (scattering methods), the state of hydration (NMR), the counterion binding (NMR), and the location of solubilized molecules in micelles (NMR).

2.2.3.1 Surface tension measurements

Seemingly very simple surface tension measurements probably constitute the most frequently employed method for determining the cmc of surfactant and block copolymer systems. The origin behind this is that surfactants/block copolymers are surface active, and tend to adsorb at numerous surfaces, and so also at the air-water interface. On increasing the surfactant/block copolymer concentration (below cmc) the adsorption increases, which results in a surface tension reduction. Once the cmc is reached, all additionally added surfactant/copolymer molecules go to the micelles, whereas the free surfactant/copolymer concentration is essentially constant, as is the adsorption and the surface tension. Ideally, therefore, a plot of

the surface tension vs. the surfactant/copolymer concentration displays a clear breakpoint, from which the cmc is readily identified (Figure 2.26).

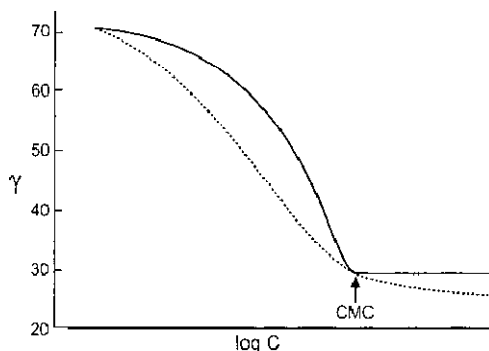


Figure 2.26. Schematic illustration of the surface tension γ of a surfactant/block copolymer versus the concentration c for a monodisperse and homogeneous sample (solid line) and a polydisperse and/or heterogeneous sample (dashed line).

In the case of polydisperse and/or heterogeneous surfactants/block copolymers the strict meaning of the cmc is lost, and also from a practical perspective determination of an effective cmc becomes more difficult. This is illustrated in Figure 2.26, where it is shown that the polydisperse/heterogeneous compound displays a more gradual decrease in the surface tension vs. concentration. Surface tension measurements are also very sensitive to the presence of hydrophobic impurities, and only an impurity level of the order of 0.1% of the surfactant may well cause a drastic deviation from the “ideal” curve displayed in Figure 2.26. The reason for this is that typical surface tension methods are based on the use of a macroscopic air-water surface (e.g., in a trough), and hence the bulk volume to surface area is large, and even minute amounts of impurities are sufficient to cause a dramatic accumulation at the interface, and hence large effects on the surface tension. From a more positive perspective, surface tension measurements constitute a critical test of the surfactant purity. If the surface tension curve looks nice, then the risk of any hydrophobic impurities is generally limited.

2.2.3.2 Light scattering

Scattering of radiation from a surfactant solution offers possibilities to characterize the solution in a number of ways. In principle, both light, X-rays, and neutrons can be used for investigations of surfactant and block copolymer micelles, but due to its simplicity, light scattering is the technique most extensively used for such investigations. In so-called static light scattering, the scattering intensity is collected at different scattering angles for a series of samples of different concentrations.

Frequently, the results are summarized in a so-called Zimm-plot, and information about the molecular weight M_w , radius of gyration R_g size, and second virial coefficient B (a measure of intermolecular interactions) is extracted from the reciprocal of the scattering intensity extrapolated to zero concentration, the angular dependence of the scattering intensity, and the concentration dependence of the scattering intensity, respectively (Figure 2.27).

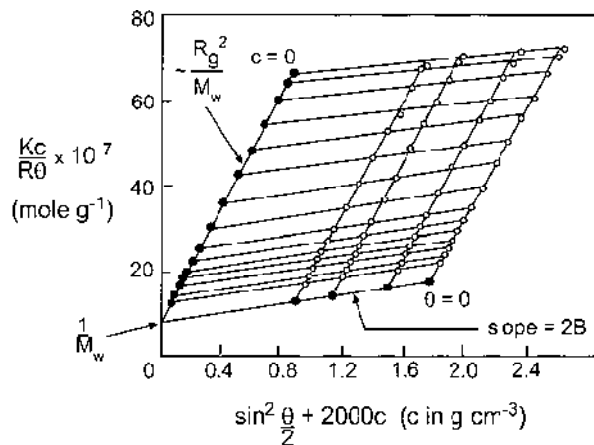


Figure 2.27. Typical Zimm-plot for static light scattering data, in which the scattering intensity is plotted as a function of concentration c and scattering angle Θ .

In dynamic light scattering (often called also photon correlation spectroscopy), the time dependence of the light intensity fluctuations is analyzed in order to yield information about the diffusion coefficient, which in turn can be used to extract a micellar hydrodynamic radius. Frequently, static and dynamic light scattering experiments are combined for a given system, which allows information to be extracted on both the micellar size, shape, and aggregation number.

2.2.3.3 NMR

Since both the microenvironment of a nucleus of a surfactant molecule and the overall mass transport properties change on micellization, NMR offers many opportunities when it comes to investigating both micellization and the properties of micellar systems. Probably the most extensively used of these is NMR selfdiffusion measurements. Such measurements have several advantages:

1. A true self-diffusion coefficient is obtained.
2. No chemical labeling is required, and possible artefacts relating to fluorescence or radioactive labels can therefore be avoided.
3. The self-diffusion of essentially any number of components in a mixture can be followed simultaneously.

4. In contrast to, e.g., light scattering, there are no restrictions relating to optical clarity of the sample and use of dilute samples.
5. In contrast to experiments where the diffusion coefficient is determined through following the concentration gradient of the diffusing species, NMR self-diffusion measurements are fast.

In the case of micellizing surfactants, self-diffusion measurements contain information on both free molecules and molecules in the micellar state. For low molecular weight surfactants, the micellar residence time is generally very short on the NMR time scale (~ 100 ms), which means that there is extensive molecular exchange during an NMR experiment, and therefore the observed diffusion coefficient D_{obs} determined by NMR constitutes an average over the two states, i.e.,

$$D_{\text{obs}} = p_{\text{mic}}D_{\text{mic}} + p_{\text{free}}D_{\text{free}} \quad (2.1)$$

where D_i and p_i are the diffusion coefficient and the fraction in state i . Since the diffusion coefficients of the free surfactant molecules can be determined from measurements below the cmc, since the diffusion coefficient of the micelles may be obtained through measurement of the diffusion coefficient of a hydrophobic molecule solubilized in the micellar core, and since the total concentration is known, the concentration of micelles and free surfactant molecules can be extracted. Furthermore, by simultaneously measuring the surfactant and counterion self-diffusion in the case of ionic surfactants, information about the degree of counterion binding, i.e., the fraction of counterions bound to the micelles, can be estimated. A typical result from such an analysis is shown in Figure 2.28.

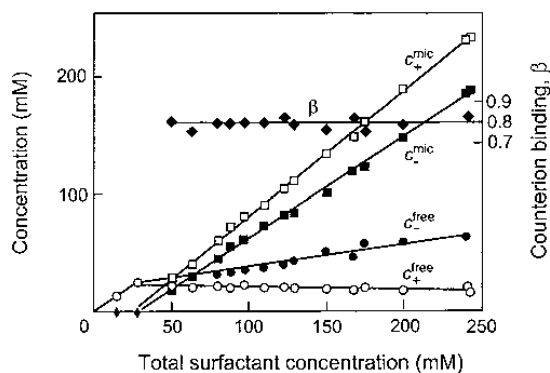


Figure 2.28. Concentrations of micellar (squares) and free (circles) surfactant molecules (open symbols), and counterions (filled symbols), as well as the degree of counterion binding (filled diamonds), as a function of the total surfactant concentration. The surfactant used was decylammonium dichloroacetate.

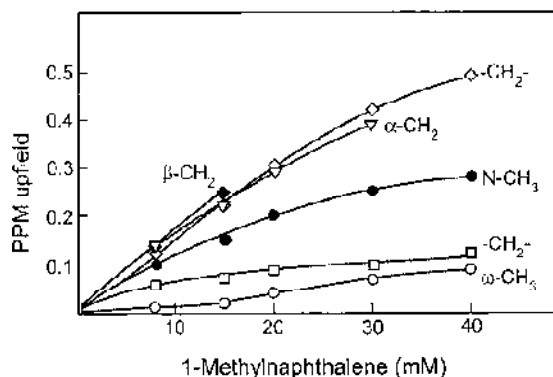


Figure 2.29. Effect of 1-methylnaphthalene on the chemical shift of CTAB protons.

From the latter type of measurement one can conclude that:

1. Above the cmc, the concentration of micelles increases largely linearly with the total surfactant concentration, whereas the free monomer concentration is either constant (nonionic surfactants) or decreases somewhat (ionic surfactants).
2. Below the cmc, all surfactant molecules are in a nonmicellized form.
3. The degree of counterion binding for ionic surfactants is generally quite high (~ 70 – 90%).

Apart from self-diffusion measurements, there are also several other NMR techniques which may be used in order to characterize micellar systems. For example, measuring the chemical shift of surfactant molecules may provide information about both the extent of water penetration into the micellar core, and the precise location of solubilized molecules in micelles. As an example of the latter, Figure 2.29 shows the effect of an aromatic solubilisate, 1-methylnaphthalene, on the chemical shift of cetyltrimethylammunium bromide (CTAB) protons. As can be seen, the protons in the polar head group (α -, β -) of the surfactant experience a larger chemical shift than protons closer to the micellar core (ω -), which shows that the solubilisate is located close to the polar head groups, i.e., close to the micellar surface.

2.3 Emulsion polymerization

In an emulsion polymerisation process vinyl or acrylic monomers are converted into a water-dispersed polymer (latex). The process starts with the help of a freeradical initiator. The polymer particles are stabilised with surface active materials (surfactants) to prevent undesired fusion or coagulation. The final product is a polymer latex. The emulsion polymerisation process has various advantages

compared to bulk or solution polymerisation as it proceeds at low viscosity. This allows an adequate removal of the heat of reaction generated during the process and the production of high molar mass polymers in combination with high monomer conversion and short cycle-times. The final product is a water-based system with a low viscosity. The emulsion polymerisation process is applied on an industrial scale for the production of latices used as binders in a variety of products such as emulsions paints, adhesives, primers and sealers.

2.3.1 Description of process

2.3.1.1 Utility

Emulsion polymerization was first employed during World War II for producing synthetic rubbers from 1,3-butadiene and styrene. This was the start of the synthetic rubber industry in the United States. It was a dramatic development because the Japanese naval forces threatened access to the natural-rubber (NR) sources, which were necessary for the war effort. Synthetic rubber has advanced significantly from the first days of “balloon” tires, which had a useful life of 5000 mi to present-day tires, which are good for 50,000 mi. Emulsion polymerization is presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylate copolymerizations, and copolymerizations of butadiene with styrene and acrylonitrile. It is also used for methacrylates, vinyl chloride, acrylamide, and some fluorinated ethylenes.

The emulsion polymerization process has several distinct advantages. The physical state of emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerizations. The product of an emulsion polymerization, referred to as a *latex*, can in many instances be used directly without further separations. (However, there may be the need for appropriate blending operations, e.g., for the addition of pigments.) such applications include paints, coatings, finishes, and floor polishes. Aside from the physical difference between the emulsion and other polymerization processes, there is one very significant kinetic difference. For the other processes there is an inverse relationship between the polymerization rate and the polymer molecular weight. This drastically limits one's ability to make large changes in the molecular weight of a polymer, from 25,000 to 100,000 or from 100,000 to 25,000. Large decreases in the molecular weight of a polymer can be made without altering the polymerization rate by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords the means of increasing

the polymer molecular weight without decreasing the polymerization rate. Because of a different reaction mechanism, emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

2.3.1.2 Qualitative picture

Components and their locations

The physical picture of emulsion polymerization is based on the original qualitative picture of Harkins [1947] and the quantitative treatment of Smith and Ewart [1948] with subsequent contributions by other workers. Table 2.1 shows a typical recipe for an emulsion polymerization. This formulation, one of the early ones employed for the production of styrene-1,3-butadiene rubber (trade name: GR-S), is typical of all emulsion polymerization systems. The main components are the monomer(s), dispersing medium, emulsifier, and water-soluble initiator. The dispersing medium is the liquid, usually water, in which the various components are dispersed by means of the emulsifier. The ratio of water to monomer(s) is generally in the range 70/30 to 40/60 (by weight).

The action of the emulsifier (also referred to as surfactant or soap) is due to its molecules having both hydrophilic and hydrophobic segments. Various other components may also be present in the emulsion system. Thus, a mercaptan is used in the above formulation as a chain transfer agent to control the polymer molecular weight. The initiator is the hydroperoxide-ferrous ion redox system and the function of fructose is probably to generate ferrous ion by reducing the ferric ion produced in the initiation reaction. The sodium pyrophosphate acts to solubilize the iron salts in the strongly alkaline reaction medium. The emulsion system is usually kept in a well-agitated state during reaction.

Table 2.1. Composition of a GR-S Recipe for Emulsion Polymerization of Styrene-Butadiene^a

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (Dresinate 731)	5
n-Dodecyl mercaptan	0,5
NaOH	0,061
Cumene hydroperoxide	0,17
FeSO ₄	0,017
Na ₄ P ₂ O ₇ ·10H ₂ O	1,5
Fructose	0,5

^aData from Vanderberg and Hulse [1948].

The locations of the various components in an emulsion system will now be considered. When the concentration of a surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as micelles. The transformation of a solution to the colloidal state as the surfactant concentration exceeds the CMC occurs to minimize the free energy of solution (heat is liberated) and is accompanied by a sharp drop in the surface tension of the solution. Electrical conductivity, ion activities, viscosity, and the other solution properties also shown marked changes at CMC. CMC values are in the range 0.001-0.1 mole/liter, with most surfactants having values in the lower end of the range. Since surfactant concentrations in the emulsion polymerization (0.1-3 wt% based on the aqueous phase) exceed CMC by one or more orders of magnitude, the bulk of the surfactant is in the micelles. Typical micelles have dimensions of 2-10 nm (1nm: $10 \text{ \AA} = 10^{-3} \text{ \mu m}$) with each micelle containing 50-150 surfactant molecules. Most authors show the shape of micelles as being spherical, but this is not always the case. Both spherical and rod-like micelles are observed depending on the surfactant and its concentration. The surfactant molecules are arranged in a micelles and their size depends on the amount of emulsifier. Large amounts of emulsifier yield larger numbers of smaller-sized particles.

When a water-soluble or slightly water-soluble monomer added, a very small fraction dissolves in the continuous aqueous phase. The water solubilities of most monomers are quite low, although the spread is large; for example, styrene, butadiene, vinyl chloride, methyl methacrylate, and vinyl acetate are soluble to the extent of 0.07, 0.8, 7, 16, 25 g/liter, respectively, at 25°C. An additional but still small portion of the monomer enters the interior hydrocarbon portions of the micelles. This is evidenced by X-ray and light-scattering measurements showing that the micelles increase in size an monomer is added. The amount of monomer in micelles compared to that in solution is much greater for the water-insoluble, nonpolar monomers. For example, the amount of micellar monomer is 2-, 5-, and 40-fold larger for methyl methacrylate, butadiene, and styrene, respectively, than the amount in solution. For vinyl acetate, the amount of micellar monomer is only a few percent of that in solution.

The largest portion of the monomer (>95%) is dispersed as monomer droplets whose size depends on the stirring rate. The monomer droplets are stabilized by surfactant molecules absorbed on their surfaces. Monomer droplets have diameters in the range 1-10 μm (10^3 - 10^4 nm) or larger. Thus, in a typical emulsion

polymerization system, the monomer droplets are much larger than the monomer-containing micelles. Consequently, while the concentration of micelles is 10^{17} - 10^{18} per millimeter, there are at most 10^{10} - 10^{11} monomer droplets per millimeter. A further difference between micelles is larger than that of the droplets by more than two orders of magnitude. The size, shape, and concentration of each of the various types of particles in the emulsion system are obtained from electron microscopy, light scattering, ultracentrifugation, photon correlation spectroscopy, and other techniques.

The different phases of the emulsion polymerisation process

At the start of the process, the monomers are dispersed into small droplets, stabilised by surfactants. Most of the remaining surfactant molecules are present as clusters (micelles) in the water phase (Figure 2.30). These micelles are very small (10 nm) relative to the monomer droplets (1-10 μm). Three different stages of emulsion polymerisation can be distinguished. During stage I the initial formation of polymer particles takes place. In stage II the polymerisation proceeds with a constant supply of new monomer which results in growth of the polymer particles. At the end of stage II monomer supply ceases and subsequently the rate of polymerisation decreases gradually (stage III).

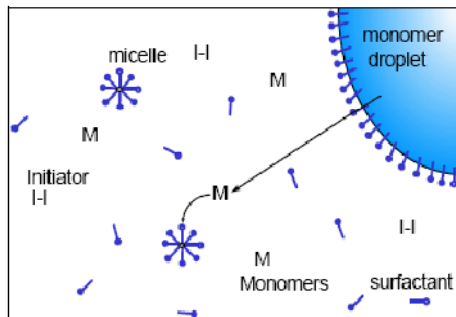


Figure 2.30. Initial situation

To begin with the reactor is charged with water, surfactants and part of the initiator. The reactor is heated to the reaction temperature. Typically 5 to 10% of the total amount of monomers are subsequently added to the reactor to produce a so-called in-situ seed latex which allows better control of the particle formation step. The polymerisation is started by the initiator generating free radicals by thermal decomposition in the aqueous phase. The free radicals react with monomers present in the water phase to form oligomer chains (stage I). These oligomers can be absorbed into the micelles or can continue to grow and adsorb surfactant molecules. In either case this results in the formation of new polymer particles

(Figure 2.31). This process continues until no micelles are left. In the case of a semi-continuous process, stage I corresponds with the generation of the seed latex.

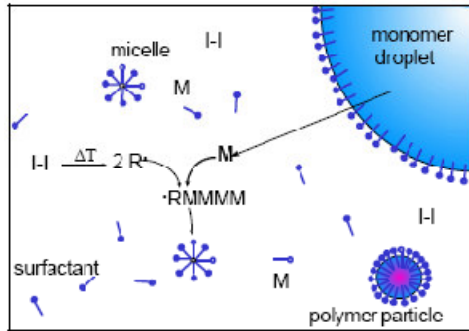


Figure 2.31. Stage I of the emulsion polymerization process

The polymer particles start to absorb additional monomer which migrates from the monomer droplets through the water phase. The polymerisation then proceeds mainly in the monomer-swollen polymer particles without the formation of new particles (stage II). The monomers consumed by polymer chain growth are replaced by new monomers which continue to migrate from the monomer droplets (Figure 2.32). Depletion of monomer droplets is prevented by the continuous addition of new monomers. The growing particles are stabilised by adsorption and/or grafting of surfactants and colloids onto their surface. Fresh initiator is continuously added to the reactor via a separate initiator feed stream. For a semi-continuous process, stage II applies during the monomer addition period.

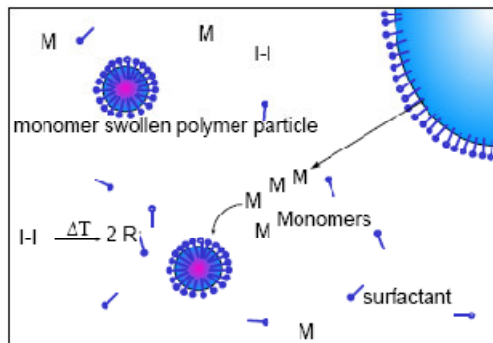


Figure 2.32. Stage II of the emulsion polymerization process

When all the monomers have been added to the reactor, the polymerisation continues with the conversion of residual monomer in the polymer particles. Gradually the rate of polymerisation decreases to zero when no residual monomer is left (Figure 2.33). Stage III corresponds with the post-cooking period applied at the end of the semi-continuous process.

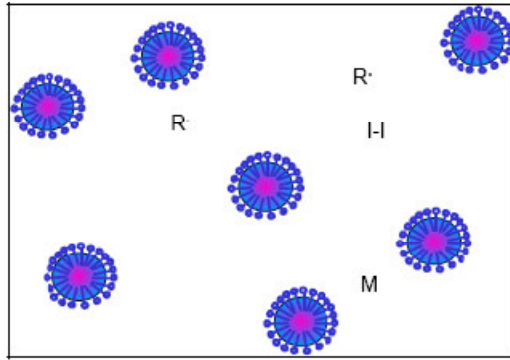


Figure 2.33. Stage II of the emulsion polymerization process

Stabilisation of the latex

There are two forms of stabilisation that prevent premature coagulation of latex particles:

- **Electrostatic repulsion** between the polymer particles. This can be provided by means of anionic surfactants and negatively charged functional groups located at the polymer/water interface.
- **Steric stabilisation** by hydrophilic groups located at the surface of the polymer particles. These hydrophilic groups originate from non-ionic surfactants or protective colloids. They attract much water, thus creating a so-called protective water-barrier between the particles that prevents coagulation.

Electrostatic stabilisation is complementary to steric stabilisation. The two are therefore usually combined to achieve the optimum result. If protective colloids are used, normally in combination with surfactants, the latex is referred to as a colloid-stabilised latex. If protective colloids are absent, the latex is called a colloid-free latex. Idealised structures of a colloid-stabilised and colloid-free latices are given in Figure 2.34.

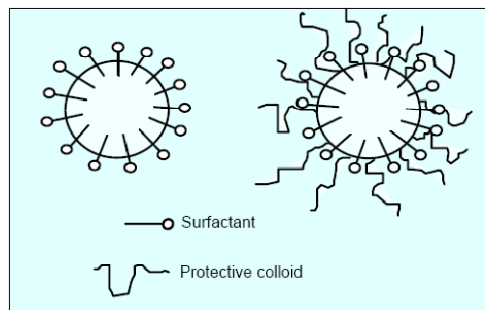


Figure 2.34. Idealized structures of a colloid-free and colloid-stabilised latex particle.

Progress of Polymerization

A variety of behaviours are observed for the polymerization rate versus conversion depending on the relative rates of initiation, propagation, and termination, which are in turn dependent on the monomer and reaction conditions (Figure 2.35).

Irrespective of the particular behavior observed, three intervals (I, II, III) can be discerned in all emulsion polymerization based on the particle number N (the concentration of polymer particles in units of number of particle per millimeter) and the existence of a separate monomer phase (i.e., monomer droplets).

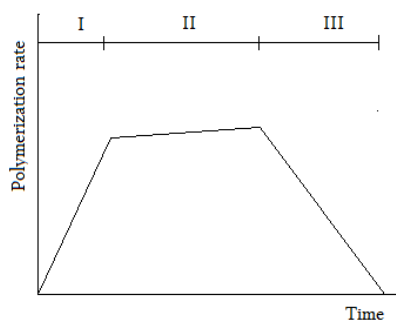


Figure 2.35. Different rate behaviours observed in emulsion polymerization.

There is a separate monomer phase in intervals I and II but not in III. The particle number increases with time in interval I and then remains constant during intervals II and III. Particle nucleation occurs in interval I with the polymerization rate increasing with time as the particle number builds up. Monomer diffuses into the polymer particles to replace that which has reacted. The reaction system undergoes a very significant change during interval I. The particle number stabilizes at some value which is only a small fraction, typically about 0.1%, of the concentration of micelles initially present. (N is in range 10^{13} - 10^{15} particles per millimeter.) As the polymer particles grow in size and contain polymer as well as monomer, they absorb more and more surfactant (in order to maintain stability) from that which is in solution. The point is quickly reached at which the surfactant concentration in solution falls below its CMC, the inactive micelles interval I or very early in interval II all or almost all of the surfactant in the system has been absorbed by the polymer particles. As a consequence the monomer droplets are relatively unstable and will coalesce if agitation is stopped. Interval I is generally the shortest of the three intervals, its duration varying in the range 2-15% conversion. Interval I is longer for low initiation rates as more time is needed to attain the steady state particle number. The more water-soluble monomers such as vinyl acetate tend to complete interval I faster than the less water-soluble monomers. This is probably a consequence of the significant

extent of homogenous nucleation occurring simultaneously with micellar nucleation, resulting in achieving the steady-state particle number sooner. The predicted maximum in Figure 2.35 (Interval I), arising from a transient high particle number and/or high proportion of particles containing propagating radicals, is often not distinguishable experimentally, since it is not a high maximum. The maximum is observed for many monomers when the initiation rates are sufficiently high.

Polymerization proceeds in the polymer particles as the monomer concentration in the particles is maintained at the equilibrium (saturation) level by diffusion of monomer from solution, which in turn is maintained at the saturated level by dissolution of monomer from the monomer droplets. The monomer concentration in the polymer particles is high; the volume fraction of monomer Φ_m is 0.2, 0.3, 0.5, 0.6, 0.71, and 0.85 for ethylene, vinyl chloride, butadiene, styrene, methyl methacrylate, and vinyl acetate, respectively. The polymerization rate either is constant or increases slightly with time during Interval II. The latter behaviour, which may begin immediately as shown in Figure 2.35 or after a constant rate period, is a consequence of the gel or Trommsdorff effect. The polymer particles increase in size as the monomer droplets decrease. Interval II ends when the monomer droplets disappear. The transition from Interval II to III occurs at lower conversions as the water solubility of the monomer increases and the extent of swelling of the polymer particles by monomer increases. For monomers (e.g., vinyl chloride) with low water solubility and low Φ_m , the transition occurs at about 70-80% conversion. The transition occurs at progressively lower conversion as the proportion of the total monomer in the system that is contained in the droplets decreases; styrene and butadiene at 40-50% conversion. methyl methacrylate at 25%, and vinyl acetate at 15%. The particle number remains the same in Interval III as in Interval II but the monomer concentration decreases with time, since monomer droplets are no longer present. The decrease in Φ_m is slower with the more water-soluble monomers as the monomer in solution acts as a reservoir. The presence of a gel effect continues in Interval III. The quantitative interplay of a decreasing monomer concentration with the gel effect determines the exact behaviour observed in this interval. Polymerization continues at a steadily decreasing rate as the monomer concentration in the polymer particles decreases. Final conversions of essentially 100% are usually achieved. The final polymer particles, spherical in shape, usually have diameters of 50-200 nm, which places them intermediate in size between the initial micelles and monomer droplets. (Polymer particles as small as 10 nm and as high as several μ m have been produced in emulsion polymerization.)

2.3.2 Main ingredients in latices

2.3.2.1 Initiators

The initiators used in emulsion polymerization are water-soluble initiators such as potassium or ammonium persulfate, hydrogen peroxide, and 2,2'-azobis(2-amidino-propane) dihydrochloride. Partially water-soluble peroxides such as succinic acid peroxide and t-butyl hydroperoxide and azo compounds such as 4,4'-azobis(4-cyanopentanoic acid) have also been used. Redox systems such as persulfate with ferrous ion are commonly used. Redox systems are advantageous in yielding desirable initiation rates at temperatures below 50°C. Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite, or bisulfite ion.

The usual initiator for vinyl acetate polymerization is potassium persulphate. Ammonium persulphate is also sometimes used, as well as redox systems that allow lower reaction temperatures. The amount of initiator should be sufficient to provide an adequate number of free radicals. In colloid-stabilised latices, too high amounts of free radicals should be avoided as this can cause excessive degradation of the protective colloid and hence a reduction of the latex viscosity. Using too much initiator also produces polymers with a low molecular weight. This usually leads to lower mechanical performance. The partition of the initiator between the initial reactor charge and the initiator feed is also important. Good results are usually obtained using the minor part in the initial reactor charge and the major part in the initiator feed stream.

Following the addition of the monomer mixture to the reactor, it is common practice to add extra initiator or a redox booster during the post-cooking period to achieve high monomer conversion.

2.3.2.2 Surfactants

Anionic surfactants are the most commonly used surfactants in emulsion polymerization. These include fatty acid soaps (sodium or potassium stearate, laurate, pelmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate). The sulfates and sulfonates are useful for polymerization in acidic medium where fatty acid soaps are unstable or where the final product must be stable toward either acid or heavy-metal ions. Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjunction with anionic surfactants for improving

the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution. The presence of the nonionic surfactant imparts a second mode of colloidal stabilization, in addition to electrostatic stabilization by the anionic surfactant, via steric interference with the Van der Waals attraction between polymer particles. Nonionic surfactants are also of use where the final polymer latex should be insensitive to changes in pH over a wide range. Nonionic surfactants are only infrequently used alone, since their efficiency in producing stable emulsions is less than that of the anionic surfactants. Anionic surfactants are generally used at a level of 0.2 - 3 wt% based on the amount of water; nonionic surfactants are used at the 2 - 10 % level.

Cationic surfactants such as dodecylammonium chloride and cetyltrimethylammonium bromide are much less frequently used than anionic surfactants because of their inefficient emulsifying action or adverse effects on initiator decomposition. Also, cationic surfactants are more expensive than anionic surfactants.

Surfactants increase particle number and decrease particle size as their concentration in the initial reaction charge is increased. However, one can use delayed addition of surfactant after nucleation is complete to improve particle stability, without affecting the particle number, size and size distribution.

Surfactants and protective colloids

Surfactants play an essential role in providing good stability both during the emulsion polymerisation process and during storage and transport. By choosing specific types and amounts of surfactants the average particle size of the latex can be controlled to a large extent. Surfactants also have an effect on many performance properties of the latex, such as pigment binding power and water sensitivity. Finally, some surfactant types are less favoured for health and safety reasons. It is therefore important to pay some extra attention in choosing the right surfactant types. Anionic surfactants provide shear stability to the latex during the polymerisation reaction. They enable small particles to be formed and minimise losses by coagulation. Non-ionic surfactants provide electrolyte stability and contribute to mechanical and freeze-thaw stability. The use of either surfactant type alone is insufficient; latices prepared using only anionic surfactants are usually deficient in electrolyte stability whereas high coagulation losses may occur when only non-ionic surfactants are used.

A combination of dodecyl benzene sulphonate as the anionic surfactant with a suitable non-ionic surfactant delivers stable latices with good performance. Nonyl phenol ethoxylates have been the standard type non-ionic surfactants for many years, but they are now under environmental pressure. Alternatives have been selected from a wide range of non-ionic surfactants with various chemical structures. Many latices use a protective colloid for stabilization (between 0.5% and 2% on monomer weight) in addition to a combination of surfactants. The colloid can have an effect on the emulsion polymerization process because it reacts with radicals.

3. EXPERIMENTAL

3.1 Materials

All the chemicals, Tetramethylethylene diamine (TEMED) (Fluka), Dibromohexane (Fluka), Vinyl acetate (VAc) (Fluka), Methyl methacrylate (MMA) (Fluka), Diethylether (E.Merck), Ammonium persulfate (Fluka) were analytical grade chemicals. They were used as supplied.

3.2 Instruments

KSV model 701 Tensiometer, Pt ring

Brookfield viscometer model DVII (programmable – spindle)

FT-IR (Perkin Elmer spectrum one)

Conductometer (WTW)

3.3 Preparation of Polymeric Surfactant

5 ml of TEMED was added to 20 mL of Diethylether and 5,2 mL of Dibromohexane was added to this solution. The reaction was proceeded at room temperature for 48 h. Precipitated white solid product was filtered and was washed with excess of diethylether to remove soluble fractions. The white polymeric product was dried under vacuum at room temperature for 24 h. The yield was 10,33 g (86 %). The polymeric surfactant was characterized by using FT-IR spectroscopy, critical micelle measurements and viscosity measurement.

3.3.1 Determination of the critical micelle concentration (CMC)

For this purpose 0,5 g of polymeric surfactant sample was dissolved in 30 mL water. This solution was placed in thermostat bath at 25°C. 1 mL of water at a time was added to the surfactant solution until the volume reaches up to 50 mL and conductivity of the solution was measured after every addition continuously.

3.3.2 Viscosity measurements

1,03 g of the polymeric surfactant was dissolved in 100 mL of water and Ubbelohde viscometer was used for viscosity measurements. 15 mL of solution was placed in viscometer and viscosity measurement was performed at 25°C. Four different surfactant concentrations were used to obtain inherent viscosity value. Also viscosity measurements were performed in different ionic strength. All results were given in Table 4.1.

3.4 Emulsion polymerization of MMA and VAc

Polymerization reactions were performed by using different surfactant concentration and initiator concentrations. The polymerizations were performed at 70°C for VAc and at 85°C for MMA for different time depending on the surfactant quantity. Obtained polymers were precipitated by adding NaCl and polymers were filtered and washed with excess of hot water and methanol. The polymers were dried under vacuum at room temperature for 24 h. After polymerization, surface tension and viscosity measurements of the latexes were investigated. All results were given in Table 4.2, 4.3, 4.4, 4.5.

Table 3.1 Recipe for the emulsion polymerization of VAc using the polymeric surfactant

Substance	Use
Vinyl acetate	Monomer
Polymeric surfactant	Achieving the stability of latexes
Ammonium persulfate	Thermal initiator
Water	Media

Emulsion polymerization of MMA was carried out at 85°C for different time, surfactant concentration and initiator quantity.

Table 3.2. Recipe for the emulsion polymerization of MMA using the polymeric surfactant

Substance	Use
Methyl methacrylate	Monomer
Polymeric surfactant	Achieving the stability of latexes
Ammonium persulfate	Thermal initiator
Water	Media

3.5. Measurements

New synthesized polymeric surfactant was characterized by FT-IR and its critical micelle concentration was determined by conductometric methods. Latexes were characterized by measuring Brookfield viscosity, viscosity average molecular weight (M_v), and surface tension of latexes to air.

Conversions were monitored gravimetrically. The original viscosities of the homopolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 20°C. Viscosity average molecular weights (M_v) of polymers were determined by capillary intrinsic viscometry at 30°C. M_v values of the polymers were determined using Ubbelohde-type viscometer in an acetone solvent for poly(vinyl acetate) and poly(methyl methacrylate). Mark-Houwink constant values of VAc were used as $\alpha=0,72$ and $K=1.01 \times 10^{-4}$ (dL/g) and MMA were used as $\alpha=0,69$ and $K=9,6 \times 10^{-3}$ (dL/g) in the calculations. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinum ring at 23.7°C.

3.5. Determination of the molecular weight of polymers

Stable latexes were precipitated by adding salt and obtained polymers were filtered and was washed excess of hot water and were dried under vacuum at room temperature for 48 h. Dried polymers were dissolved in different concentration by using acetone for PVAc and PMMA.

Molecular weight of the polymers were determined viscosimetrically by using Mark-Houwink-Sakurada equation:

$$[\eta]=K.M_v^\alpha \quad (3.1)$$

All results were given in Table 4.2, 4.3, 4.4, 4.5.

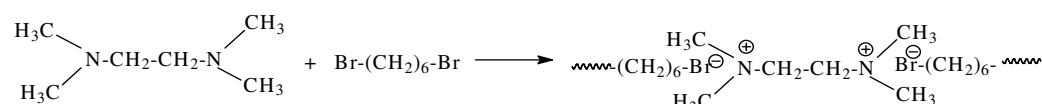
4. RESULTS AND DISCUSSION

4.1 Measurements of the polymeric surfactant

4.1.1 Preparation of Polymeric Surfactant

Polymeric surfactant was prepared by starting from TEMED and 1,6-Dibromohexane. The reaction was carried out in Ether at room temperature for 3 days. White precipitated solid product was filtrated and was washed with excess of ether.

The polymeric product was characterized by FT-IR , viscosity measurements and critical micelle concentration.



Scheme 4.1 Schematic illustration of reaction between TEMED and Dibromohexane

The FT-IR spectrum of cationic surfactant (Figure 4.1) was as expected, with bands for the alkyl group at 2900–2800 cm^{-1} . If FT-IR spectrum of surfactant was compared with TEMED (Spectral Database for Organic Compounds, SDBS No: 2373) new bands were observed at 1133 cm^{-1} and 3010 cm^{-1} because of quaternization.

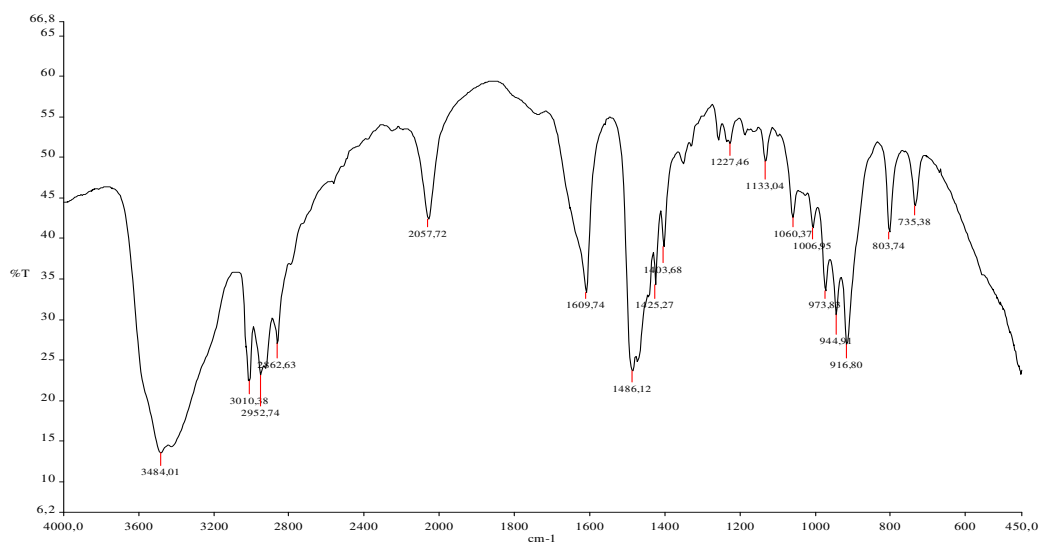


Figure 4.1 The FT-IR spectrum of the polymeric surfactant

4.1.2 Determination of CMC of the polymeric surfactant.

Critical micelle concentration of the surfactant was determined by conductometric measurements. This value was calculated from Figure 4.2 as 1.67×10^{-2} g/mL.

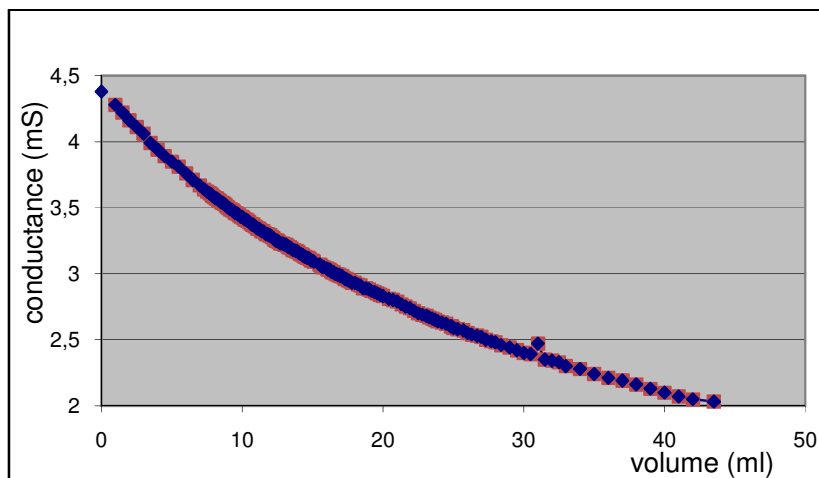


Figure 4.2 The CMC graph of the polymeric surfactant.

4.1.3 Viscosity of polymeric surfactant

The inherent viscosities of the polymeric surfactant in various solutions calculated from the data taken from the Ubbelohde type viscometer.

Table 4.1 Inherent viscosity values in different solutions.

Polymeric surfactant in :	Inherent viscosity
Water	12,4
1 M KBr	0,71
1 M HBr	0,58

4.2 Preparation of emulsion polymers

Emulsion polymerizations of Methyl methacrylate and Vinyl acetate with polymeric surfactant was carried out in a 250 mL glass reactor equipped with a condenser and a mechanical stirrer having a constant speed of 400 rpm.

4.2.1 Measurements of the emulsion polymers

Stable latexes were precipitated by adding salt and obtained polymers were filtered and washed excess of hot water and were dried under vacuum at room temperature for 48 h. Dried polymers were dissolved in different concentration by using acetone for PVAc and PMMA.

4.2.1.1 Characterization of the emulsion polymers

Molecular weights of the polymers were determined viscosimetrically by using Mark-Houwink-Sakurada equation. Emulsion polymerization of MMA was carried out kinetically at constant surfactant quantity. According the results in Table 4.2, molecular weights of MMA increased with increasing reaction time.

Table 4.2 The results from the viscometric measurements of the emulsion polymerization of methyl methacrylate changing with reaction time at constant Monomer amount

Surfactant Quantity	Reaction time	Solvent	t (sec)	η_r	η_{sp}	c	η_{sp}/c	Mv
MMA 0,942 g/l	1 h	0 ml	1293	29,38	28,38	0,014	2027,61	275.000
		5 ml	1086	24,68	23,68	0,011	2152,89	
		10 ml	563	12,79	11,79	0,009	1325,33	
		15 ml	367	8,34	7,34	0,007	1048,71	
MMA 0,942 g/l	2 h	0 ml	798	18,13	17,13	0,016	1071,02	400.000
		5 ml	583	13,25	12,25	0,012	1020,83	
		10 ml	338	7,68	6,68	0,009	742,42	
		15 ml	214	4,86	3,86	0,008	482,95	
MMA 0,942 g/l	3 h	0 ml	169	3,84	2,84	0,015	189,39	477.000
		5 ml	128	2,91	1,91	0,012	166,01	
		10 ml	114	2,59	1,59	0,011	165,72	
		15 ml	91	2,04	1,04	0,008	130,68	
MMA 0,942 g/l	5 h	0 ml	62	1,75	0,75	0,006	125,01	498.000
		5 ml	58	1,61	0,61	0,005	122,71	
		10 ml	56	1,52	0,52	0,004	121,97	
		15 ml	54	1,38	0,38	0,003	103,03	

Also, emulsion polymerization of MMA was carried out in constant monomer concentration and time depending on surfactant quantity. According to the Table 4.3 and Table 4.4, molecular weight of PMMA decreases with increasing surfactant quantity.

Table 4.3 The results from the viscometric measurements of the emulsion polymerization of methyl methacrylate changing with Surfactant value at constant reaction time.

Surfactant Quantity	Reaction time	Solvent	t (sec)	η_r	η_{sp}	c	η_{sp}/c	Mv
MMA 0,942 g/l 0,5 g Surfactant	3 h	0 ml	169	3,84	2,84	0,015	189,39	498.000
		5 ml	128	2,91	1,91	0,012	166,01	
		10 ml	114	2,59	1,59	0,011	165,72	
		15 ml	91	2,04	1,04	0,008	130,68	
MMA 0,942 g/l 0,6 g Surfactant	3 h	0 ml	197	4,47	3,47	0,016	217,33	458.000
		5 ml	172	3,91	2,91	0,012	242,42	
		10 ml	108	2,45	1,45	0,01	151,52	
		15 ml	97	2,21	1,21	0,008	150,57	
MMA 0,942 g/l 0,7 g Surfactant	3 h	0 ml	524	14,18	13,18	0,016	814,91	413.000
		5 ml	404	10,08	9,08	0,012	749,33	
		10 ml	295	6,55	5,55	0,011	571,37	
		15 ml	266	4,27	3,27	0,008	404,64	

Table 4.4 The results from the viscometric measurements of the emulsion polymerization of methyl methacrylate changing with Surfactant amount at constant reaction time and initiator amount

Surfactant Quantity	Reaction time	Solvent	t (sec)	η_r	η_{sp}	c	η_{sp}/c	Mv
5 ml Surfactant MMA 0,942 mol/l 1 g APS	1,5 h	0 ml	182	4,13	3,13	0,016	192,84	540.000
		5 ml	148	3,36	2,36	0,014	174,4	
		10 ml	128	2,91	1,91	0,012	164,33	
		15 ml	112	2,55	1,55	0,01	152,04	
10 ml Surfactant MMA 0,942 mol/l 1 g APS	1,5 h	0 ml	186	6,51	5,51	0,015	361,84	435.000
		5 ml	160	3,63	2,63	0,011	231,84	
		10 ml	142	3,22	2,22	0,009	244,22	
		15 ml	118	2,68	1,68	0,008	221,29	
20 ml Surfactant MMA 0,942 mol/l 1 g APS	1,5 h	0 ml	338	7,68	6,68	0,016	417,61	420.000
		5 ml	244	5,55	4,55	0,012	378,79	
		10 ml	201	4,57	3,57	0,01	371,69	
		15 ml	110	2,51	1,51	0,008	187,51	

Also, different initiator quantity was used in emulsion polymerization of PMMA. According to the Table 4.5, molecular weight of PMMA increased with decreasing initiator quantity.

Table 4.5 The results from the viscometric measurements of the emulsion polymerization of methyl methacrylate changing with initiator amount at constant surfactant amount and time

Surfactant Quantity	Reaction time	Solvent	t (sec)	η_r	η_{sp}	c	η_{sp}/c	Mv
0,4 g Surfactant MMA 0,942 mol/l 1 g APS	1,5 h	0 ml	168	3,81	2,81	0,016	176,14	425.000
		5 ml	132	3,02	2,02	0,012	166,67	
		10 ml	112	2,55	1,55	0,01	160,98	
		15 ml	102	1,86	0,86	0,008	107,95	
0,4 g Surfactant MMA 0,942 mol/l 0,15 g APS	1,5 h	0 ml	78	1,77	0,77	0,007	107,32	600.000
		5 ml	68	1,55	0,55	0,005	102,01	
		10 ml	63	1,43	0,43	0,004	99,96	
		15 ml	60	1,36	0,36	0,003	101,01	

From the figures below, viscosity average molecular weights of polymers were calculated for various reaction times.

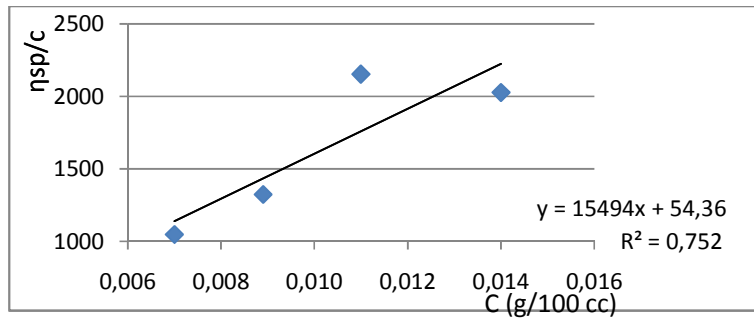


Figure 4.3 Viscosity graph of PMMA at 1 hour reaction time at constant monomer value

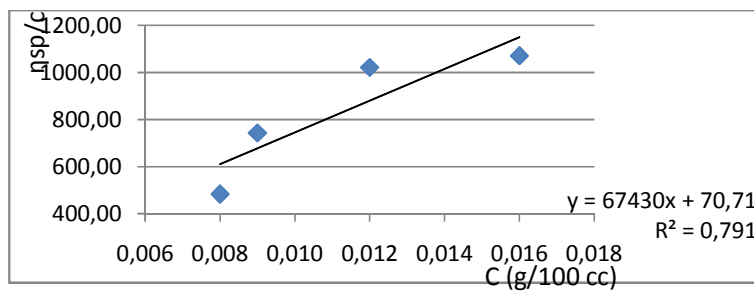


Figure 4.4 Viscosity graph of PMMA at 2 hour reaction time at constant monomer value

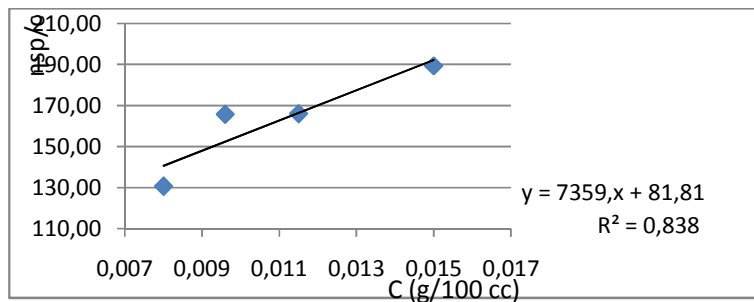


Figure 4.5 Viscosity graph of PMMA at 3 hour reaction time at constant monomer value

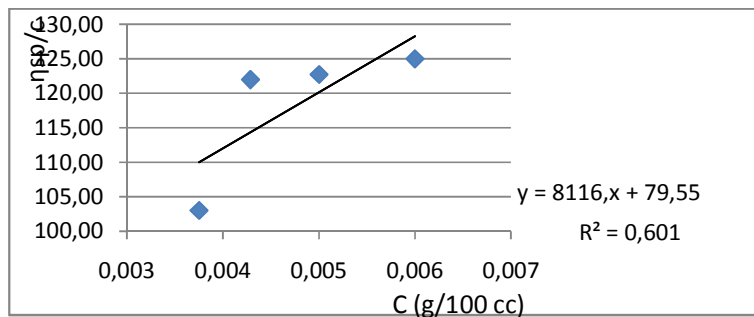


Figure 4.6 Viscosity graph of PMMA at 5 hour reaction time at constant monomer value

From the figures below, viscosity average molecular weights of polymers were calculated for various surfactant quantities..

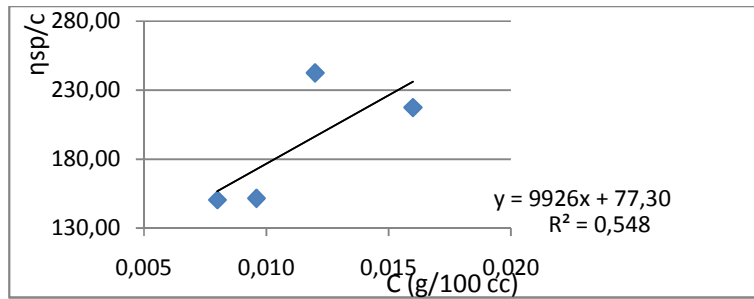


Figure 4.7 Viscosity graph of PMMA at 0,6 g surfactant value at constant reaction time

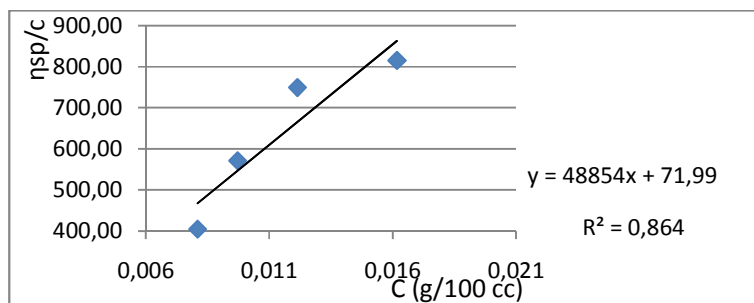


Figure 4.8 Viscosity graph of PMMA at 0,7 g surfactant value at constant reaction time

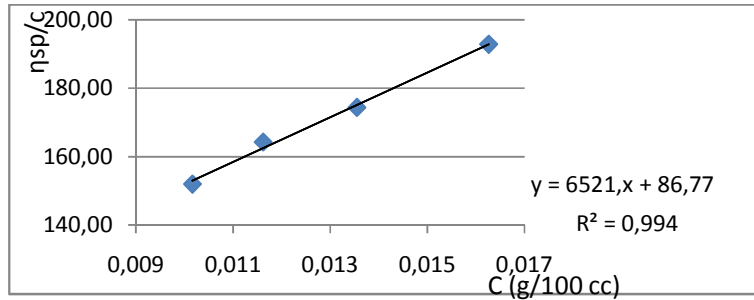


Figure 4.9 Viscosity graph of PMMA at 5 ml surfactant value at constant reaction time and initiator value.

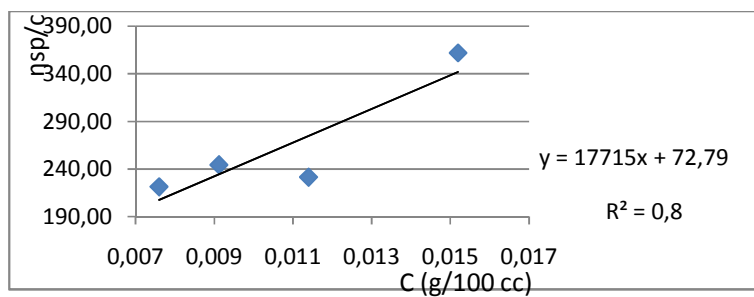


Figure 4.10 Viscosity graph of PMMA at 10 ml surfactant value at constant reaction time and initiator value.

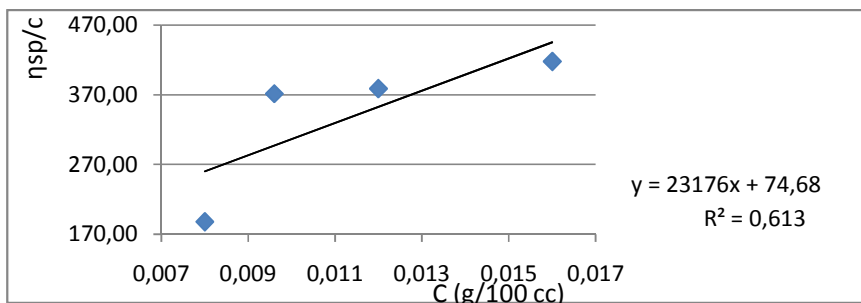


Figure 4.11 Viscosity graph of PMMA at 20 ml surfactant value at constant reaction time and initiator value.

From the figures below, viscosity average molecular weights of polymers were calculated for various initiator quantities.

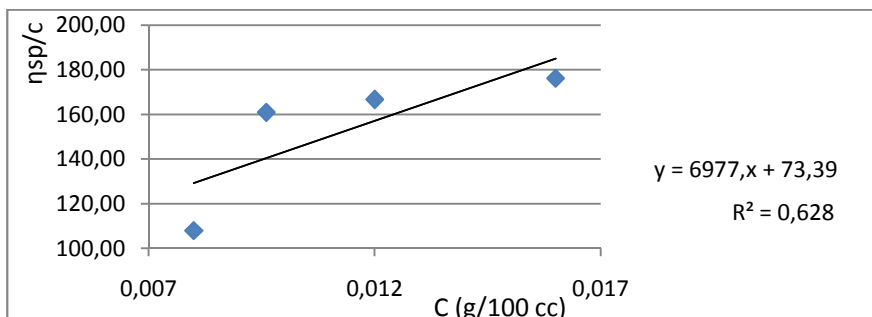


Figure 4.12 Viscosity graph of PMMA at 1 g initiator value at constant surfactant amount and time.

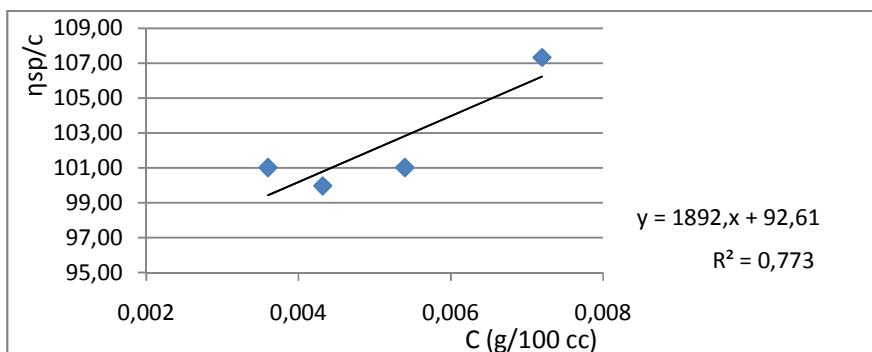


Figure 4.13 Viscosity graph of PMMA at 0,1533 g initiator value at constant surfactant amount and time.

Emulsion polymerization of VAc was also studied in different monomer concentrations. VAc is hydrophilic than MMA monomer. VAc can interacted with surfactant, therefore PVAc can be obtained stable colloid than PMMA.

Also, molecular weight of poly (vinyl acetate) is higher than poly (methyl methacrylate) because of the termination reaction differences.

Table 4.6 The results from the experiments of the emulsion polymerization of methyl methacrylate and vinyl acetate by using the cationic surfactant.

Polymer	Reaction time (h)	Surfactant quantity (g)	Initiator (g)	Brookfield viscosity (cP)	Surface tension (mN/m)	Mv
PMMA (0,942 M)	1	0,5	0,15			274.879
PMMA (0,942 M)	2	0,5	0,15			402.394
PMMA (0,942 M)	3	0,5	0,15			497.081
PMMA (0,942 M)	5	0,5	0,15			477.304
PMMA (0,942 M)	3	0,6	0,15			457.864
PMMA (0,942 M)	3	0,7	0,15			412.993
PMMA (0,928 M)	1,5	5 ml	1,00			541.347
PMMA (0,928 M)	1,5	10 ml	1,00			419.661
PMMA (0,928 M)	1,5	20 ml	1,00			435.545
PMMA (0,942 M)	1,5	0,4	1,00			424.684
PMMA (0,942 M)	1,5	0,4	0,15			594.940
PMMA (0,942 M)	3	0,3	0,15			610.645
PMMA (0,942 M)	3	0,4	0,15			457.174
PVAc (5,25 ml)	0,5	2,00	1,00	0.24	37,93	1.180.000
PVAc (10.5 ml)	0,5	2,00	1,00	0.39	40,17	2.050.000
PVAc (15,75 ml)	0,5	2,00	1,00	0.45	41,96	2.408.000

The surface tensions and Brookfield viscosity of PVAc latexes changed regularly with increasing monomer concentration.

5. CONCLUSION

In this work, a new cationic polymeric surfactant was synthesized and was used in emulsion polymerization of vinyl acetate (VAc) and Methyl methacrylate (MMA). Polymerization experiments were performed different situations.

Emulsion polymerization of MMA was investigated under different time, surfactant quantity and initiator quantity. Poly (methyl methacrylate) latexes were not stable therefore surface tension and viscosity measurements were not obtained.

Vinyl acetate is hydrophilic than methyl methacrylate monomer. Poly (vinyl acetate) can interact with surfactant. Therefore, poly (vinyl acetate) can obtain stable colloid than poly (methyl methacrylate). Also, molecular weight of poly (vinyl acetate) is higher than poly (methyl methacrylate) because of the termination reaction differences.

Polymerization kinetics of poly (methyl methacrylate) was also evaluated. Molecular weight of poly (methyl methacrylate) is increased depending on reaction time.

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