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# POLYMERIC SURFACTANTS

Irja Piirma

# POLYMERIC SURFACTANTS

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藏书章

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# Preface

Polymeric surface active materials have gained enormous popularity in the past twenty years in a variety of applications and fields of research. The most obvious and best known is the stabilization of dispersions. However, polymeric surfactants appear in a multitude of other areas of research and application and have therefore acquired many different names. Besides being called polymeric surface active agents or surfactants, these amphipathic materials, when used as dispersion stabilizers, are also called emulsifiers, detergents, or dispersants. When utilized in latex rheology control, they are called thickeners. In immiscible polymer blends, they are the compatibilizers, while in water purification and sewage treatment applications, they are the flocculants. It is obvious that the name *polymeric surfactant* is really an understatement and does not properly present the limitless capabilities of these materials in a multitude of applications.

This book was not written for the experts, but rather for scientists involved in research fields other than polymer colloids. Experience has revealed a general need for some basic understanding of this very useful but complicated field. No attempt was made to reproduce and discuss in depth extensively studied and published areas of research involving polymeric amphipathic materials. For example, there are numerous theoretical papers and a book published on stabilization of dispersions by polymeric surfactants. The purely theoretical aspects, using computer simulations, of compatibilization of incompatible polymer blends have been equally well treated.

This book attempts to provide an overview of the most important topics in the

area of polymeric surfactants, and to show examples in a variety of fields. Of the eleven chapters, two are devoted exclusively to synthesis of polymeric surfactants. This is an area where guidelines are needed and have only recently started to develop, since it has been shown that the amphipathic nature alone does not guarantee the usefulness of the compounds in applications. Colloid stability provided by polymeric surfactants in aqueous and nonaqueous systems and the phenomenon of adsorption at surfaces and interfaces are the subject of a number of chapters. The rest of the chapters give basic information on applications of polymeric amphipathic materials in a variety of fields. It is hoped that this information is useful and helpful to the newcomer.

I would like to express my sincere gratitude to all my students, past and present, for their support and helpful discussions. The literature references obtained from their term papers, laboratory reports, theses and dissertations, and other literature searches were of tremendous help. My thanks go also to a number of scientists who kindly let me have their yet unpublished manuscripts and copies of their tables and figures and who gave me other information on their research results. I am especially grateful to Professors W. L. Mattice, D. H. Napper, M. Tirrell, A. Rudin, and B. Vincent, and Drs. F. Candau and A. Paine. I would like to thank my daughter, Silvia A. Dolson, for handling all the permission requests to reprint data and figures.

Most importantly, my thanks goes to my husband, Dr. Aleksander Piirma, who ran our household while I was glued to the PC. Maybe I should start another project fast, to maintain this convenient situation.

*Irja Piirma*

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# 1
# Polymeric Surfactants and Colloid Stability

## I. INTRODUCTION TO COLLOIDAL DISPERSIONS

Colloidal dispersions are finely subdivided systems of dispersed phase in a dispersion medium. This fine subdivision creates a very high specific surface area (area per unit weight) and determines largely the physical properties of the dispersion. In the most common dispersion the continuous phase (dispersion medium) is a liquid, but it can also be a solid or a gas. To be considered a colloid, the liquid droplets or the solid particles in a liquid dispersion have to have a size in diameter between one nanometer (nm) and one micrometer (μm).

The most common dispersion is one liquid dispersed in another, and it is called an emulsion. A dispersion of a solid in a liquid has been named a sol, but when the solid is a polymer, the dispersion is a polymer colloid.

Heterophase polymerizations begin as emulsions and solutions, and, as soon as polymerization has started and polymer is formed, the system becomes a polymer colloid. Although the word dispersion is used to describe a colloidal state of one material dispersed in another, thus including emulsion, the term dispersion polymerization has been used to distinguish between two types of polymerization systems, emulsion and dispersion. Aside from polymerization kinetics, the big difference between emulsion and dispersion is that in emulsion polymerization the polymer is soluble, or at least swellable by its monomer, and the particles remain swollen throughout the reaction. The particles are mostly spherical in shape. In dispersion polymerization the polymer is not soluble in its

monomer, but precipitates as soon as it is formed. To prevent precipitation the polymer chains have to be stabilized by a surface active material. Often these polymers are crystalline, as, for example, polytetrafluoroethylene, and the particles are not spherical, but take on a variety of shapes.

In aqueous-phase emulsion polymerizations, the monomer-swollen polymer particles can be stabilized by surface groups derived from initiator fragments. But most commonly the particles are surrounded by surface active materials for stabilization.

In nature, where the continuous phase most often is water, we deal primarily with large molecules and polymeric materials in aqueous phase where they have limited solubility. These materials are usually stabilized by polymeric surface active materials. In the biological systems, where ionic strength is high, polyelectrolytes are the type of materials that provide stability to the system. In natural rubber latex, for example, the high molecular weight polyisoprene chains are stabilized by protein molecules. Milk remains a suspension because casein, a macropeptide, provides a negatively charged outer layer to the particles.

## II. COLLOID STABILITY

Unprotected particles in a dispersion will rapidly aggregate if not provided with a potential energy barrier to prevent it. The terms flocculate and coagulate have been defined by Napper [1] as representing reversible and irreversible aggregation, respectively. It has been found by theoretical calculations [2] and confirmed by experiment [3] that the rate constant of particle coagulation is rapidly halved. This means that at normal particle concentrations the number of unprotected particles is reduced by a factor of two of the original number in just a few seconds.

In order for a colloid to be stable, i.e., to remain as a fine subdivision of particles in a liquid which is a nonsolvent for the dispersed phase, it has to be stabilized. Due to Brownian motion, particles in a dispersion are in constant movement and collide with each other and the container walls. Since there is a van der Waals attraction between particles, these collisions can be "sticky." To reduce collisions leading to particle coagulation, it is necessary to provide the particles with a repulsive interaction that outweighs the attraction. Stability can be provided to colloidal particles by surrounding them with an electrical double layer (electrostatic stabilization) or by chemically attached, adsorbed, or dissolved oligomeric or polymeric materials (polymeric stabilization). These will be discussed in more detail below. Excellent treatments of the subject of colloid stabilization can be found in several books [1,4,10].

### A. Attractive Forces: Particle-Particle Interactions

The primary source of attraction between colloidal particles arises as a consequence of van der Waals forces. These van der Waals attractive forces between

molecules can have different possible sources of origin. The permanent dipole–permanent dipole (Keesom) forces and the permanent dipole–induced dipole (Debye) interactions are short-range interactions. A third, transitory dipole–transitory dipole, the so-called London dispersion forces, are long-range attractions [1,6,7].

The London dispersion forces are electrical in nature and originate from the electronic fluctuations of the atoms. The existence of dispersion forces has been demonstrated by the liquefaction, upon cooling, of such noble gases as argon and helium. These gases do not possess a permanent dipole, and therefore do not exhibit short-range attraction forces. Since these gases can be liquefied, strong intermolecular forces must be present. These dispersion forces operating between two atoms of a noble gas extend only a few angstroms. Hamaker [8] calculated the dispersion forces between colloidal particles by the summation of attractive forces between all of the atoms.

The energy of attraction $V_A$ per $cm^3$ between two spheres of equal radius was shown by Hamaker [9] to be:

$$V_A = (A'/12)[(x^2+2x)-1+(x^2+2x+1)-1+2\ln(x^2+2x/(x^2+2x+1)] \quad (1)$$

where A′, the composite Hamaker constant for the particles in the medium $= (\sqrt{A_{11}} - \sqrt{A_{22}})^2$, and $x = h/2a$, with $a$ = radius of particles and $h$ = distance of surface separation.

According to Napper [1] the long-range character of the van der Waals attraction is approximately 5–10 nm.

As was stated above, stability can be provided to colloidal particles by surrounding them (1) with an electrical double layer (electrostatic stabilization), (2) by adsorbed or chemically attached oligomeric or polymeric materials (steric stabilization), or (3) by free polymer in the dispersion medium (depletion stabilization). The last two modes of stabilization are often combined under the heading of polymeric stabilization [1].

Electrosteric stabilization utilizes both electrostatic and steric stabilization to provide effective repulsion between colloidal particles. There are basically two possible ways for such stabilization:

1. The combination of an ionic surfactant and a nonionic surface active component should provide a combination of steric and electrostatic stabilization effects. It is not quite clear whether this is really true, and there may be a predominance of one or the other depending on the circumstances.
2. The use of polyelectrolytes, where the effective repulsion is provided by electrostatic forces along the surface active polymeric chain adsorbed on or attached to the particles.

The subject of polymeric stabilization will be treated in more detail after a brief discussion of the electrostatic stabilization.

## B. Electrostatic Stabilization

To date, the most effective way to counterbalance the van der Waals attraction between colloidal particles has been to provide the particles with a potential energy barrier via Coulomb repulsion. In liquid dispersion media ionic groups can be placed on particles in a variety of ways. An equal number of counterions in the surrounding medium will maintain electroneutrality and create an electrical double layer around the particle. The thickness of this double layer is a function of the ionic strength of the dispersion medium and is determined by the Debye length, $1/\kappa$. It has been calculated [1] that for a 1:1 electrolyte with molar concentration above $10^{-2}$, the $1/\kappa$ will be decreased to below 3 nm, which will be too low for any sufficient repulsion. Hence, one great disadvantage of electrostatic stabilization of particles is its great sensitivity to electrolytes.

The theory of electrostatic stabilization of colloidal particles has been credited to two groups of scientists, Derjaguin and Landau [11] and Verwey and Overbeek [12]. This DLVO theory states that the total potential energy, $V_T$, between two particles is the sum of the van der Waals attractive potential energy, $V_A$, and the electrostatic repulsive energy, $V_R$:

$$V_T = V_A + V_R \tag{2}$$

Figure 1 illustrates the total potential energy $V_T$ as a function of separation of two colloidal particles. One maximum and two minima can be observed. As two particles approach each other, the $V_A$ increases more rapidly than does $V_R$. At this point a secondary minimum is reached which corresponds to flocculation of two particles. Flocculation is a reversible process and does not affect the overall stability of the dispersion. It is the height of the primary maximum that determines the stability of the dispersion: The higher the energy barrier the lower the probability that the particles come close enough to coalesce. The DLVO theory implies that 15 kT is a sufficient energy barrier for a stable dispersion. In a real system, there is a distribution of potential energies and some particles will have enough potential energy to overcome the energy barrier and coalesce. At close approach, the potential energy curve shows a sharp increase in $V_R$ which is due to repulsion between the electron clouds of the atoms. This energy is referred to as the Born repulsion.

## C. Polymeric Stabilization

Napper [1] points out that there are at present two different recognized mechanisms of polymeric stabilization of colloidal dispersions: steric stabilization and depletion stabilization.

In steric stabilization, particles are prevented from coagulation by attached or adsorbed macromolecules. A possible combination of electrostatic and steric stabilization is provided by polyelectrolytes (electrosteric stabilization). Poly-

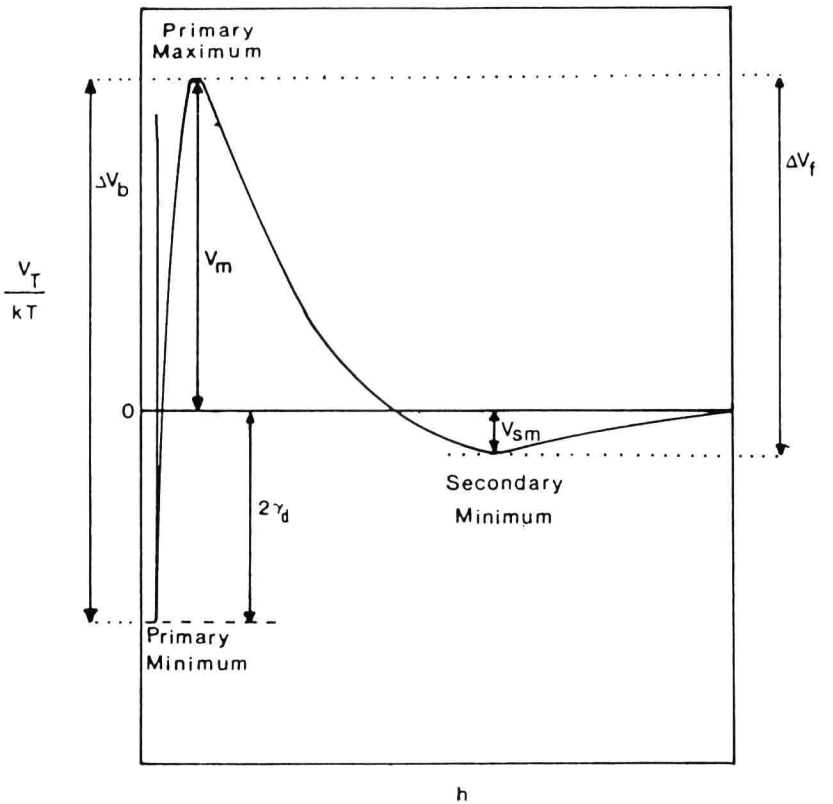


**FIG. 1** Schematic illustration of a potential energy vs distance of surface separation curve. $V_f$ = energy barrier to coagulation; $V_b$ = energy barrier to peptization; $\gamma_d$ = dispersion free energy of the polymer–water interface; $V_m$ = height of the primary maximum; $V_{sM}$ = depth of the secondary minimum. (From Ref. 9.)

peptides or protein molecules in biological systems are excellent examples of such stabilization mechanism.

Depletion stabilization is provided by unanchored, unattached polymer molecules in the dispersion phase. Polymeric molecules which would provide depletion stabilization would be homopolymers, which are soluble in the dispersion medium and do not contain any possible anchoring groups for attachment or adsorption to the colloidal particles. The most common example would be polyoxyethylene.

## 1. Steric Stabilization

In 1954, Heller and Pugh [13] were first to use the term "steric protection" to describe the stabilization of colloids by a nonionic surface active material. The

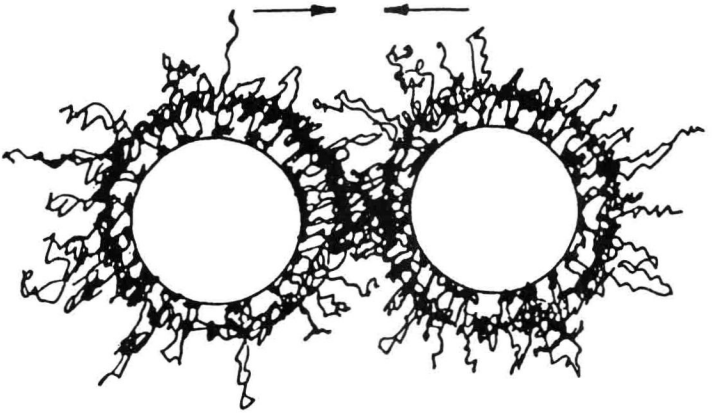

**FIG. 2** Schematic representation of steric stabilization (not to scale). (From Ref. 1.)

word "steric" as proposed by these authors does not have the same connotation as generally understood in organic chemistry, but the steric effects in the stabilization of dispersion particles have a general thermodynamic origin [1]. Heller and Pugh noted two important facts in their studies. They realized that the presence of an electrostatic charge associated with the macromolecules was not crucial, and they observed a dramatic increase in stabilizing effectiveness with increasing molecular weight of the stabilizer polymer.

Although the theory of steric stabilization of colloidal dispersions has been given considerable attention, it is still not as well understood theoretically as is electrostatic stabilization through the DLVO theory. A significant number of experimental studies have been carried out to test the proposed theories. Figure 2 shows a schematic representation of steric stabilization [1].

It has been found that the most effective steric stabilizers are amphipathic block or graft copolymers, where one part of the copolymer molecule is soluble in the dispersion medium and the other is soluble or chemically compatible with the dispersed phase. The stabilizing moieties that reach out into the dispersion medium have to be mutually repulsive in order to effectively keep the particles at a distance from each other. They have to be attached, partially absorbed, or adsorbed to the particle strongly enough as not to be desorbed from the surface when particles undergo Brownian collisions. Complete surface coverage also helps prevent escape.

The most extensively employed nonionic surfactants in aqueous dispersions have been the polymeric surfactants with polyoxyethylene as the stabilizing moiety. Ottewill and Walker [15] have shown that polyoxyethylenes with an aryl or alkyl hydrophobic anchoring group can effectively stabilize polystyrene parti-

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