# Principles of emulsion stabilization with special reference to polymeric surfactants

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## Synopsis

This overview summarizes the basic principles of emulsion stabilization with particular reference to polymeric surfactants. The main breakdown processes in emulsions are briefly described. A section is devoted to the structure of polymeric surfactants and their conformation at the interface. Particular attention is given to two polymeric surfactants that are suitable for oil-in-water (O/W) and water-in-oil (W/O) emulsions. For O/W emulsions, a hydrophobically modified inulin (HMI), obtained by grafting several alkyl groups on the backbone of the inulin (polyfructose) chain, is the most suitable. For W/O emulsions, an A-B-A block copolymer of polydroxystearic acid (PHS), the A chains, and polyethylene oxide (PEO), the B chain, is the most suitable. The conformation of both polymeric surfactants at the O/W and W/O interfaces is described. A section is devoted to the interaction between emulsion droplets containing adsorbed polymer surfactant molecules. This interaction is referred to as steric stabilization, and it is a combination of two main effects, namely, unfavorable mixing of the A chains, referred to as the mixing interaction, $G_{mix}$, and loss of configurational entropy on significant overlap of the stabilizing chains, referred to as elastic interaction, $G_{el}$. The criteria for effective steric stabilization are summarized. O/W emulsions based on HMI are described, and their stability in water and in aqueous electrolyte solutions is investigated using optical microscopy. Very stable emulsions can be produced both at room temperature and at 50°C. The reason for this high stability is described in terms of the multipoint anchoring of the polymeric surfactant (by several alkyl groups), the strong hydration of the inulin (polyfructose) chains, and the high concentration of inulin in the adsorbed layer. W/O emulsions using PHS-PEO-PHS block copolymer can be prepared at a high volume fraction of water, $\varphi$, and these emulsions remain fluid up to high $\varphi$ values (>0.6). These emulsions also remain stable for several months at room temperature and at 50°C.

The last two sections are concerned with the problems of creaming or sedimentation and phase inversion. Creaming or sedimentation can be prevented by the use of "thickeners" in the continuous phase. These molecules produce non-Newtonian systems that will have a very high residual or zero shear viscosity. The latter, which may exceed 1000 Pas, can prevent any creaming or sedimentation. Syneresis of the emulsions can also be prevented by control of the bulk (or elastic) modulus of the system. Phase inversion in O/W emulsions can also be prevented using HMI, since this polymeric surfactant is not soluble in the oil phase. As long as coalescence and Ostwald ripening are prevented, the emulsions can remain stable for very long times both at room temperature and at 50°C.

## INTRODUCTION

Many personal care and cosmetic products are formulated as oil-in-water (O/W) or water-in-oil (W/O) emulsions. These systems are only kinetically stable since the energy

required to expand the interface $\Delta A \, \gamma$ (where $\Delta A$ is the increase in surface area when the bulk oil is subdivided into small droplets and $\gamma$ is the interfacial tension), which is positive, is much higher than the entropy of dispersion $T \, \Delta S$ (where $T$ is the absolute temperature and $\Delta S$ is the increase in entropy due to the formation of a large number of droplets). From the second law of thermodynamics, the free energy of formation of the emulsion is given (1):

$$\Delta G = \Delta A \, \gamma - T \, \Delta S \tag{1}$$

With macroemulsions $\Delta A \, \gamma \gg - T \, \Delta S$, $\Delta G$ is positive, emulsification is non-spontaneous (energy is required to form the emulsion), and the system is thermodynamically unstable. This leads to a number of breakdown processes, as is schematically illustrated in Figure 1. Creaming and sedimentation may occur as a result of gravity when the density of the droplets is different from that of the medium and the droplet size is large (whereby the Brownian motion is not sufficient to overcome gravity). Flocculation may occur as a result of insufficient repulsive energy between the droplets. Ostawald ripening is due to the difference in solubility between the small and large droplets. Coalescence is the result of thinning and disruption of the liquid film between the droplets. Phase inversion may occur under conditions whereby the surfactant becomes soluble in the oil phase, and hence a W/O emulsion is produced.

In order to overcome the above-mentioned breakdown processes, a number of stabilization mechanisms are necessary such that the emulsion remains stable over a long
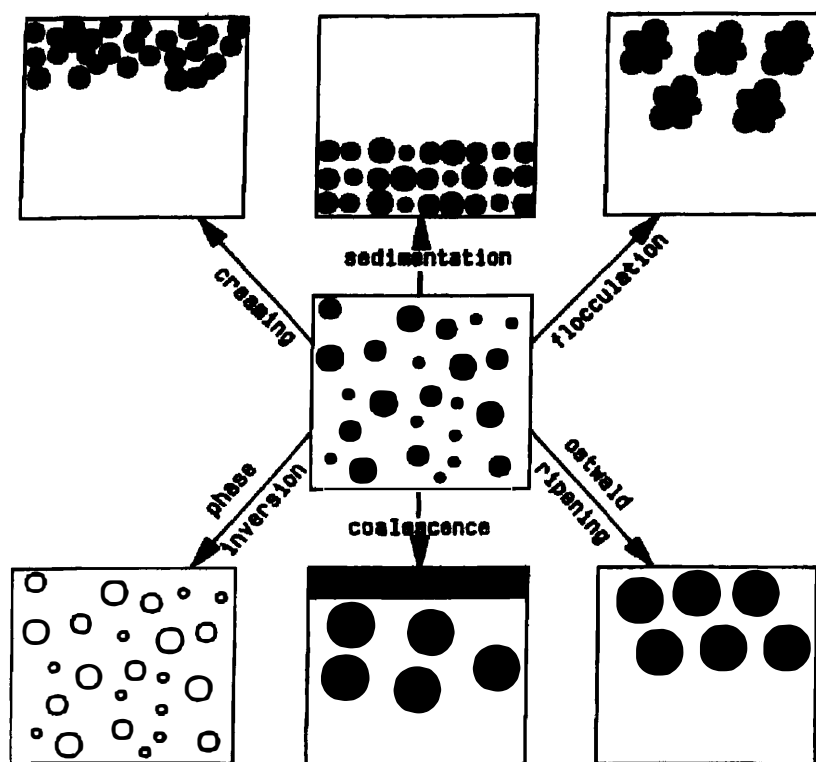


Figure 1. Schematic representation of the breakdown processes of emulsions.
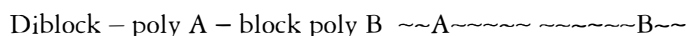
period (usually 2–3 years at various temperatures). This paper, discusses the various stabilization mechanisms that are required for prevention of strong flocculation, coalescence, and Ostwald ripening. This is best achieved using polymeric surfactants, which is the main objective of the present paper. A summary will also be given for the methods that can be applied to prevent creaming or sedimentation and phase inversion of the emulsion.

## STRUCTURE OF POLYMERIC SURFACTANTS AND THEIR CONFORMATION AT INTERFACES

The simplest type of a polymeric surfactant is a homopolymer, which is formed from the same repeating units: poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP). Homopolymers have little surface activity at the oil/water (O/W) interface. In general, homopolymers are not the most suitable emulsifiers.

A small variant is to use polymers that contain specific groups that have high affinity to the surface, e.g., partially hydrolyzed poly(vinyl acetate) (PVAc), technically referred to as poly(vinyl alcohol) (PVA). Commercially available PVA molecules contain 4–12% acetate groups. The acetate groups give the molecule its amphipathic character; on a hydrophobic surface (such as oil droplets), the polymer adsorbs with preferential attachment of the acetate groups on the surface, leaving the more hydrophilic vinyl alcohol segments dangling in the aqueous medium. Partially hydrolyzed PVA molecules exhibit surface activity at the O/W interface.

Polymeric surfactants of the block (A-B or A-B-A) or graft ($BA_n$) type are essential materials for the preparation of many emulsion systems, particularly in personal care products. A block copolymer is a linear arrangement of blocks of varying composition (2):

$$\text{Diblock} - \text{poly A} - \text{block poly B} \quad \sim\sim A\sim\sim\sim\sim\sim \ \sim\sim\sim\sim\sim\sim B\sim\sim$$

$$\text{Triblock} - \text{poly A} - \text{block poly B} - \text{poly A} \quad \sim\sim A\sim\sim\sim\sim\sim \ \sim\sim\sim\sim B\sim\sim\sim\sim \ \sim\sim\sim\sim\sim A\sim\sim$$

A graft copolymer is a non-linear array of one B block on which several A polymers are grafted:

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~~~~~ B ~~~~~
 \ \ \  \  \
 A  A  A  A  A
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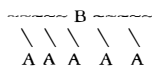
Most block and graft copolymers have low critical micelle concentrations (cmc), and in many cases it is not easy to measure the cmc for these block and graft copolymers. Several examples of block and graft copolymers may be cited: triblock polymeric surfactants; "Pluronics" (BASF) or "Synperonic PE" (ICI); and two poly-A blocks of PEO and one block poly-B of polypropylene oxide (PPO). Several chain lengths of PEO and PPO are available. Triblocks of PPO-PEO-PEO (inverse "Pluronics") are also available. Polymeric triblock surfactants can be applied as emulsifiers and dispersants. The hydrophobic PPO chain resides at the hydrophobic surface, leaving the two PEO chains dangling in aqueous solution (providing steric stabilization).

The above-mentioned triblocks are not the most efficient emulsifiers, and the PPO chain is not sufficiently hydrophobic to provide a strong "anchor" to an oil droplet. The reason

for the surface activity of the PEO-PPO-PEO triblock at the O/W interface is probably "rejection" anchoring. The PPO chain is not soluble in water or most oils.

Several other di- and tri-block copolymers have been synthesized: diblocks of polystyrene block-polyvinyl alcohol; triblocks of poly(methylmethacrylate)-block polyethylene oxide-poly(methyl methacrylate); diblocks of polystyrene-polyethylene oxide; and triblocks of polyethylene oxide-polystyrene-polyethylene oxide.

An alternative (and perhaps more efficient) polymeric surfactant is the amphipathic graft copolymer consisting of a polymeric backbone B (polystyrene or polymethyl methacrylate) and several A chains ("teeth") such as polyethylene oxide. The graft copolymer is referred to as a "comb" stabilizer, and the polymer forms a "brush" at the O/W interface. The copolymer is usually prepared by grafting a macromonomer such as methoxy polyethylene oxide methacrylate with polymethyl methacrylate. Typical commercially available graft copolymers are Atlox 4913 and Hypermer CG-6 supplied by ICI. The "grafting into" technique has also been used to synthesize polystyrene-polyethylene oxide graft copolymers. These molecules are not commercially available, and they are not approved for use in personal care and cosmetic preparations.

Recently a novel graft copolymer based on a naturally occurring polysaccharide, inulin (polyfructose), has been synthesized (3). Inulin is a polydisperse polysaccharide consisting mainly, if not exclusively, of $\beta(2\text{-}>1)$ fructosyl fructose units ($F_m$) with normally, but not necessarily, one glucopyranose unit at the reducing end ($GF_n$) (4,5). To produce the amphipathic graft copolymer, the chains were modified by introduction of alkyl groups ($C_4 - C_{18}$) on the polyfructose backbone. The structure of the molecule (hydroponically modified inulin, HMI) is illustrated in Figure 2.

In this structure, the alkyl groups represent the B chains (that are randomly distributed on the sugar backbone on primary hydroxyl functions as well as on the secondary ones), which become strongly adsorbed on an oil droplet. The sugar chain forms the stabilizing chain, as this is highly water-soluble. These graft copolymers are surface-active, and they lower the surface tension of water and the interfacial tension at the oil/water interface.
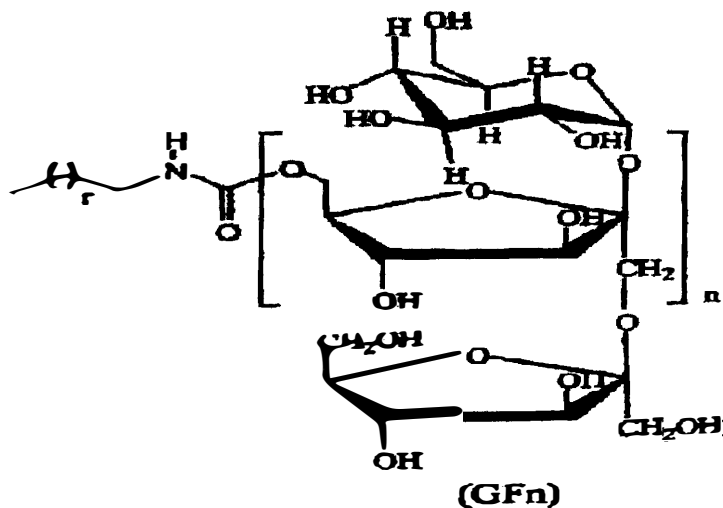


**Figure 2.** Structure of hydrophobically midfield inulin (HMI).

They will also adsorb on the oil droplets with the alkyl groups strongly attached (multipoint anchoring), leaving the polyfructose chains dangling in solution and probably forming large loops. As we will see later, these graft copolymers can produce highly stable emulsions, in particular at high electrolyte concentrations. An example of commercially available HMI is INUTEC® SP1 (produced by Orafti, Belgium).

Another A-B-A block copolymer for stabilization of W/O emulsions has been developed by Uniqema (ICI), namely Arlacel P135 (6). The A chains are poly(12-hydroxy stearic acid) (PHS), whereas the B chain is poly(ethylene oxide (PEO), i.e., PHS-PEO-PHS. A schematic representation of the structure of the polymer is given in Figure 3.

The polymer has a weight average molecular weight, $M_w$, of 6809 and an average molecular weight, $M_n$, of 3499 (polydispersity of 1.94). It has an HLB number of 5–6, which makes it suitable for W/O emulsions. The PHS chains (the stabilizing chains) are highly soluble in most hydrocarbon solvents and strongly solvated by their molecules. These chains extend in the oil, giving a layer thickness of the order of 10 nm. This makes the molecule ideal for steric stabilization (see below). The PEO chain (the "anchor chain") is highly soluble in water and in moderate electrolyte solutions, and this gives very strong adsorption at the W/O interface.

Understanding the adsorption and conformation of polymeric surfactants at interfaces is key to knowing how these molecules act as stabilizers. Most basic ideas on adsorption and conformation of polymers have been developed for the solid/liquid interface (7). The same concepts may be applied to the liquid/liquid interface, with some modification whereby some parts of the molecule may reside within the oil phase, rather than simply staying at the interface. Such modification does not alter the basic concepts, particularly when one deals with stabilization by these molecules.

The process of polymer adsorption involves a number of interactions that must be separately considered. Three main interactions must be taken into account, namely, the interaction of the solvent molecules with the oil in the case of O/W emulsions, which need to be displaced for the polymer segments to adsorb, the interaction between the chains and the solvent, and the interaction between the polymer and the surface. Apart from knowing these interactions, one of the most fundamental considerations is the conformation of the polymer molecule at the interface. These molecules adopt various conformations, depending on their structure. A schematic representation of the confor-
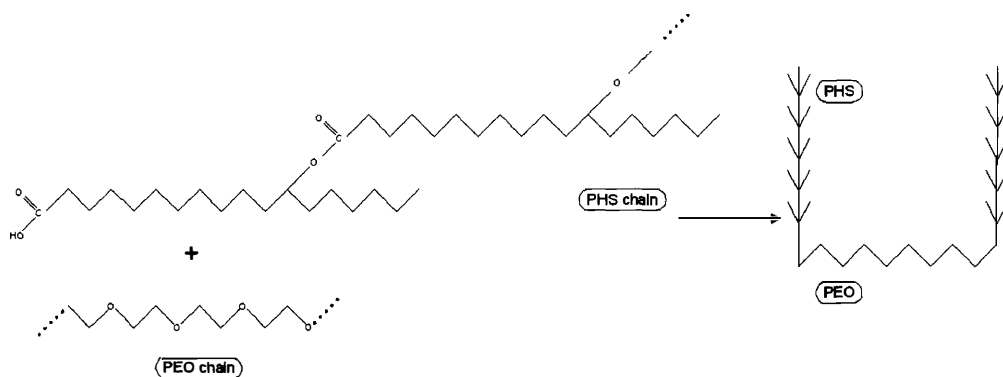


**Figure 3.** Schematic representation of the structure of PHS-PEO-PHS block copolymer.
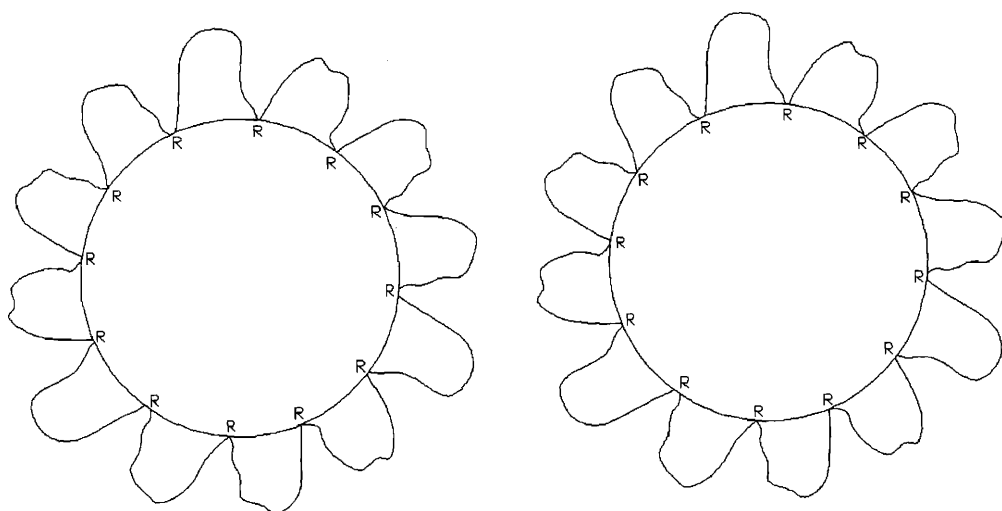
**Figure 4.** Conformation of hydrophobically modified inulin (HMI) at the O/W interface. The alkyl chains are soluble in the oil, and the polyfructose loops extend into the aqueous phase.

mation of HMI at the O/W interface is given in Figure 4, whereas that of PHS-PEO at the W/O interface is given in Figure 5.

It is clear from the above description of polymer configurations that for full characterization of the process of adsorption, it is necessary to know the following parameters, namely, the amount of polymer adsorbed per unit area of the surface, $\Gamma$ (mole m$^{-2}$ or mg m$^{-2}$), the fraction of segments in close contact with the surface, p, and the distribution of polymer segments, $\rho(z)$, from the surface towards the bulk solution. It is essential to know how far the segments extend into the solution, i.e., the thickness of the adsorbed layer. It is important to know how these parameters change with polymer overage (concentration), the structure of the polymer, and its molecular weight. It is also essen-
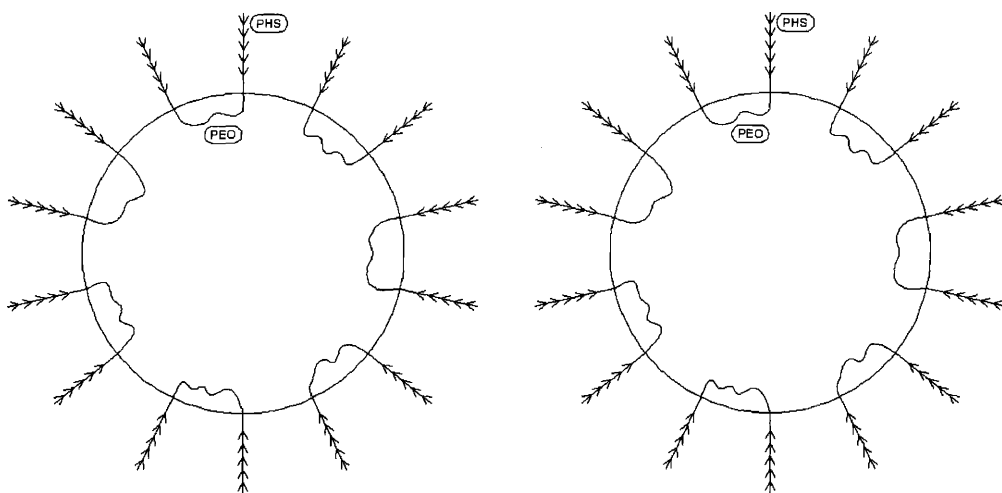


**Figure 5.** Conformation of PHS-PEO-PHS block copolymer at the W/O interface. The PEO chains are soluble in the water droplets, and the PHS chains extend into the oil phase.

tial to know how these parameters change with the environment, in such aspects as solvency of the medium for the chains and temperature.

## INTERACTION BETWEEN DROPLETS CONTAINING ADSORBED POLYMER LAYERS (STERIC STABILIZATION)

When two droplets containing adsorbed polymer layers (with an adsorbed layer thickness, $\delta$) approach a distance of separation, h, whereby these layers begin to overlap, i.e., when h < 2$\delta$, repulsion occurs as a result of two main effects (8). The first repulsive force arises from the unfavorable mixing of the polymer layers when these are present in a good solvent (i.e., the chains are strongly solvated by the medium). The unfavorable mixing of polymer solutions in good solvent conditions was considered by Flory (9), whose theory was applied to the present case of interparticle interaction. A schematic representation of the mixing of polymer layers on close approach is shown in Figure 6, which shows the situation when two droplets with polymer layers are forced to approach a distance, h, that is less than 2$\delta$, forming an overlap region with a volume element, dV. Before overlap, the chains have a volume fraction, $\varphi_2$, and the solvent has a chemical potential, $\mu_1^{\alpha}$. In the overlap region, the volume fraction of the chains is $\varphi_2'$, which is higher than $\varphi_2$, and the solvent has a chemical potential, $\mu_1^{\beta}$, which is lower than $\mu_1^{\alpha}$. This is equivalent to an increase in the osmotic pressure in the overlap region. As a result, solvent diffuses from the bulk to the overlap region and the two particles or droplets are separated, i.e. this results in strong repulsion. The latter is referred to as mixing or osmotic repulsion.

Using the Flory-Krigbaum theory (9), one can calculate the free energy of mixing, $G_{mix}$, due to this unfavorable overlap, i.e.,

$$\frac{G_{mix}}{kT} = \frac{4\pi}{3V_1} \phi_2^2 N_{av} \left(\frac{1}{2} - \chi\right) \left(\delta - \frac{h}{2}\right)^2 \left(3R + 2\delta + \frac{h}{2}\right) \qquad (2)$$
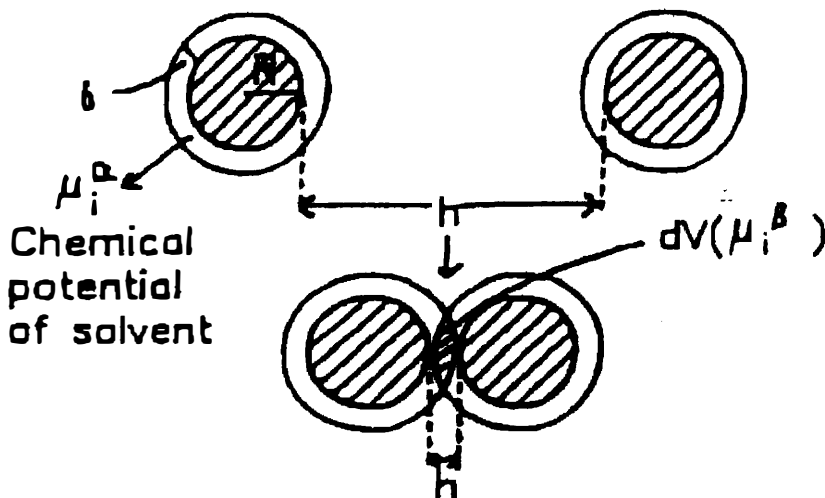


**Figure 6.** Schematic representation of the overlap of two polymer layers.

where k is the Boltzmann constant, T is the absolute temperature, $V_1$ is the molar volume of the solvent, and $N_{av}$ is the Avogadros's constant. $\chi$ is a dimensionless quantity that gives a measure of the polymer–solvent interaction, i.e., the solvation of the A chains by the molecules of the medium. It is referred to as the Floury-Huggins interaction parameter.

It is clear from equation 2 that when the Flory-Huggins interaction parameter, $\chi$, is less than 0.5, the chains are in good solvent conditions, $G_{mix}$ is positive, and the interaction is repulsive and increases very rapidly with decreasing h, when the latter is lower than $2\delta$. This explains why the hydrophobically modified inulin (HMI) polymeric surfactant is ideal for stabilizing O/W emulsions. In this case the polyfructose loops are strongly hydrated by water molecules. For stabilization of W/O emulsions, the stabilizing chains have to be soluble in the oil phase (normally a hydrocarbon). In this case, poly(hydroxystearic acid) (PHS) chains are ideal. A polymeric surfactant of PHS-PEO-PHS (Arlacel P135) is an ideal W/O emulsifier.

Equation 2 also shows that when $\chi > 0.5$, i.e., when the solvency of the medium for the chains becomes poor, $G_{mix}$ is negative and the interaction becomes attractive. The condition $\chi = 0.5$ is referred to as $\theta$-solvent, in which case mixing of the chains with the solvent does not lead to an increase or decrease of the free energy of the system (i.e., polymer mixing behaves as ideal). The $\theta$-condition denotes the onset of change of repulsion to attraction. Thus, to ensure steric stabilization by the above mechanism, one has to ensure that the chains are kept in better than a $\theta$-solvent.

The second repulsive force arises from the loss of configurational entropy when the chains overlap. This is schematically illustrated in Figure 7, whereby the polymer chain is represented by a simple rod with one attachment point to the surface. When the two surfaces are separated at infinite distance, each chain will have a number of configurations, $\Omega_\infty$, that are determined by the volume of the hemisphere swept by the rod. When the two surfaces approach a distance, h, that is smaller than the radius of the hemisphere swept by the rod, the volume available to the chains becomes smaller and this results in a reduction in the configurational entropy to a value, $\Omega$ (which is less than $\Omega_\infty$). This results in strong repulsion, and the effect is referred to as entropic, volume restriction or elastic repulsion, and is given by the following expression (8):

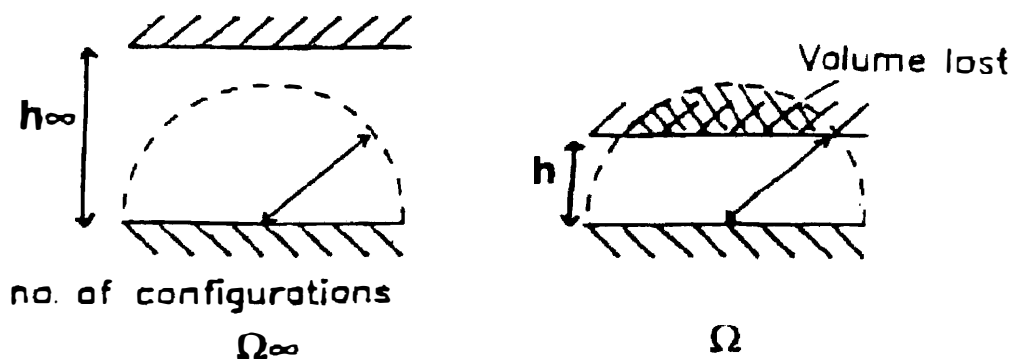$$G_{el} = 2v \ln \frac{\Omega}{\Omega_\infty} \tag{3}$$



Figure 7. Schematic representation of the entropic, volume restriction or elastic interaction.

where $\nu$ is the number of polymer chains per unit area of the surface. It should be mentioned that $G_{el}$ is always repulsive and becomes very high on considerable overlap of the polymer chains.

Plots of $G_{mix}$ and $G_{el}$ versus h are illustrated in Figure 8. This figure shows that $G_{mix}$ increases very rapidly with a decrease in h as soon as h becomes smaller than $2\delta$ (and $\chi$ < 0.5). $G_{el}$ also increases very rapidly with a decrease in h on further overlap. Combination of $G_{mix}$, $G_{el}$, and $G_A$ (the van der Waals attraction) results in the total $G_T$ – h curve shown in Figure 8. This curve shows a minimum ($G_{min}$) at h ~ $2\delta$, but when h < $2\delta$, $G_T$ increases very rapidly with a further decrease in h. The depth of the minimum, $G_{min}$, depends on the adsorbed layer thickness. With an increase of $\delta$, $G_{min}$ decreases, and at sufficiently high values of $\delta$ (of the order of 5–10 nm), it reaches small values (fraction of kT units). This shows that with sterically stabilized dispersions, there is only weak attraction at relatively long distances of separation, which in most cases is overcome by Brownian diffusion. Thus, one can say that the net interaction is repulsive, and this ensures the long-term stability of the emulsion.

From the above discussion one can summarize the main criteria for effective steric stabilization. First, there should be enough polymer to ensure complete coverage of the surface by the chains. This will prevent any attraction between the bare patches or bridging by the polymer chains (which can adsorb simultaneously on more than one particle). Secondly, the chains must be strongly adsorbed ("anchored") to the surface. This prevents any displacement on close approach. In this respect, block and graft copolymers containing an anchoring chain (such as the alkyl groups of HMI) for oil droplets are the best stabilizers. The third criteria for effective steric stabilization is to ensure that the stabilizing A chain remains in good solvent condition at all times and
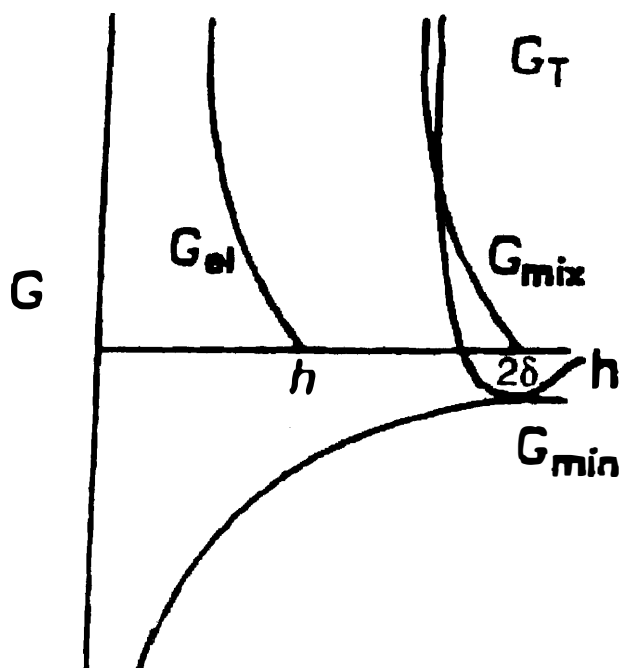


**Figure 8.** Schematic representation of the variation of $G_{mix}$, $G_{el}$, $G_A$, and $G_T$ with h.

under all conditions. As discussed above, for systems where water is the continuous medium, polyfructose (inulin) is the most suitable A chain. This polymer chain is highly soluble in water and remains solvated up to high temperatures. It can also tolerate reasonable amounts of electrolyte. For dispersions, where the continuous medium is a hydrocarbon oil (e.g., W/O emulsions) poly(hydroxystearic acid) is the most suitable A chain(s). The last criterion for effective stearic stabilization is to have a sufficiently thick adsorbed layer to avoid any weak flocculation. This is particularly important for concentrated emulsions. A value of $\delta$ of the order of 5–10 nm is usually sufficient.

## O/W EMULSION STABILIZATION USING HYDROPHOBICALLY MODIFIED INULIN (HMI) BASED POLYMERIC SURFACTANT

As mentioned above, the graft copolymer based on inulin (hydrophilic polyfructose chain) on which several alkyl groups have been grafted (INUTEC® SP1) was recently evaluated as an effective stabilizer for O/W emulsions. This polymeric surfactant was prepared using inulin (INUTEC® N25) with a degree of polymerization greater than 23. The inulin chains were hydrophobically modified by grafting several alkyl chains on the inulin backbone. Two oils, Isopar M (supplied by Exxon) and cyclomethicone (supplied by Dow Corning) were used to prepare the O/W emulsions (10). Most emulsions consisted of 50/50 (v/v) ratio oil in water, and the polymeric surfactant concentration was changed from 0.25 (w/v)% to 2 (w/v)%. The emulsions were prepared using a high-speed stirrer, an Ultra-Turrax (CAT X620). The emulsion quality was assessed by optical microscopy. Samples of the emulsions were stored at room temperature and at 50°C, and the droplet size was qualitatively assessed by taking optical micrographs at various intervals of time.

Figure 9 shows typical micrographs of diluted 50/50 Isopar M/water emulsions containing 2 (w/v)% INUTEC® surfactant that were stored for periods of 1.5 and 14 weeks at 50°C. As can be seen, there is no apparent increase in droplet size during this storage time, and this was taken as an index of stability against coalescence. Similar results were



A                                        B
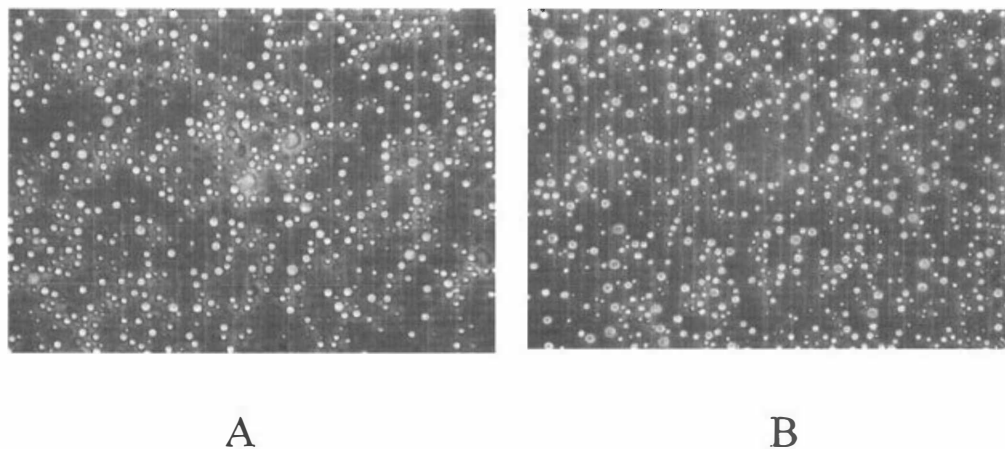
**Figure 9.** Optical micrographs of diluted 50/50 Ispoar M/water emulsions containing 2(w/v)% INUTEC® SP1 that were stored at 50°C for 1.5 (A) and 14 (B) weeks.

also obtained for emulsions stored at room temperature. No oil separation was detected after this period at RT and 50°C.

In order to evaluate the minimum polymeric surfactant that is required to prepare a stable emulsion, systems (50/50 O/W) were prepared at 0.25, 0.3, 0.4, 0.5, 1, 1.5, and 2%. All the samples were assessed for stability using the procedure described above. All emulsions containing >0.5 (w/v)% polymeric surfactant remained stable both at room temperature and 50°C. These samples did not show any apparent oil separation even after storage for 10 months at 50°C. Based on these results, it was shown that for 50/50 (v/v) O/W emulsions, an emulsifier concentration in the region of 0.5 (w/v)% is sufficient for stabilization. This is about an order of magnitude lower than the concentration used with conventional surfactants (such as alcohol ethoxylates).

Emulsions were prepared at 0.5, 1.0, and 2 mol dm$^{-3}$ NaCl, as well as in the presence of 0.5, 1.0, 1.5, and 2 mol dm$^{-3}$ MgSO$_4$. All emulsions containing NaCl did not show any coalescence up to 50°C for almost one year of storage. With MgSO$_4$, the emulsions were also stable up to 1.0 mol dm$^{-3}$.

The above-mentioned stability in high electrolyte concentrations is not observed with polymeric surfactants containing poly(ethylene oxide) (PEO) as the stabilizing chain. The difference between the inulin- and PEO-containing chains can be understood if one considers the repulsive energy obtained using these polymeric surfactants. As discussed previously, the mixing free energy, G$_{mix}$, for two droplets stabilized by A chains with thickness δ depends on the value of (1/2 – χ) (see equation 2). As discussed previously, when (1/2 – χ) is positive, i.e., χ < 1/2, G$_{mix}$ is positive and the net interaction is repulsive. If χ > 1/2, G$_{mix}$ is negative, and this leads to incipient flocculation that is normally accompanied by coalescence of the emulsion.

The Flory-Huggins interaction parameter χ is related to the solvency of the medium for the chains. In water, both inulin and PEO are strongly hydrated by the water molecules, and hence χ < 1/2 under these conditions. On increasing the temperature, H-bonds between the chains and water molecules will be broken and the χ parameter will increase. However, with both inulin and PEO, this will happen at much higher temperatures than those experienced on storage (usually the χ parameter is less than 1/2 below 80°C). With inulin, it does not show any dehydration up to 100°C.

On addition of electrolytes, dehydration of the chains may take place (salting-out effect), and at a given electrolyte concentration (and type) and temperature, χ will change value from < 1/2 to > 1/2 and G$_{mix}$ will change sign from positive to negative. It seems that the inulin-stabilizing chain can retain its hydration to much higher temperatures and electrolyte concentrations when compared to PEO chains, and this is probably the reason for the higher stability obtained when using the hydrophobically modified inulin as an emulsion stabilizer.

To confirm the above-mentioned effects, we have carried out cloud point measurements for PEO with 4000 molecular weight in the presence of various concentrations of NaCl and MgSO$_4$. Some results were also obtained for a PEO with a molecular weight of 20000 in the presence of NaCl. For comparison, results were also obtained for inulin (INUTEC® N25) in the presence of NaCl and MgSO$_4$.
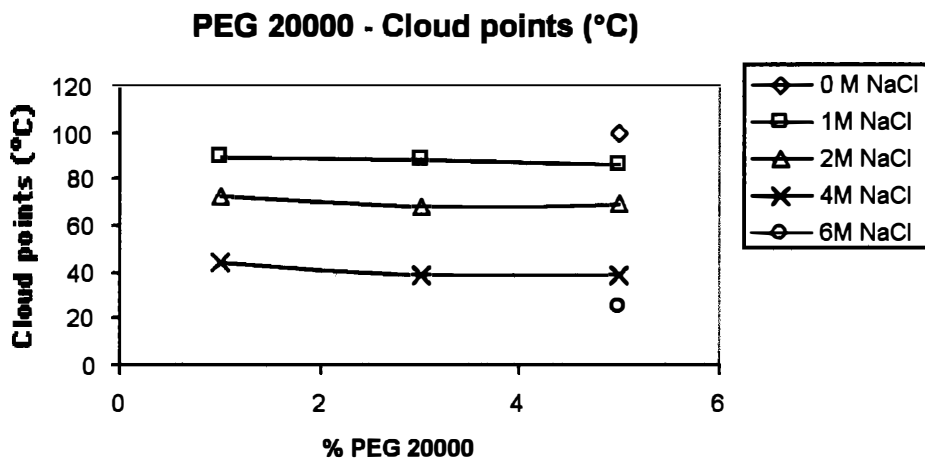
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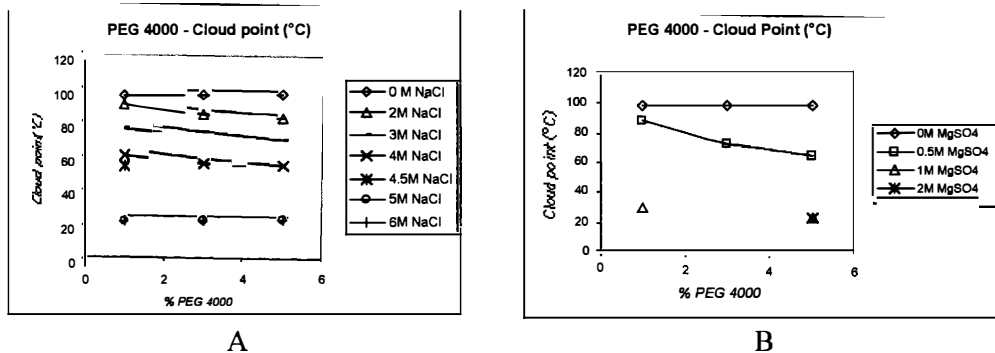
**Figure 10.** Cloud points of PEO 4000 at various NaCl (A) and MgSO$_4$ (B) concentrations as a function of PEO concentrations. Cloud points of 100°C mean that no cloud point could be noticed up to this temperature.

Figures 10A and 10B show the results for the cloud points of PEO 4000 at various concentrations of NaCl and MgSO$_4$, whereas Figure 11 shows the results for PEO 20000. The results for inulin (INUTEC® N25) are shown in Figure 12.

It can be seen from the results of Figure 10 that for PEO 4000 in water, the cloud point is around 100°C and it shows very little dependence on concentration (in the range 1–5%). On addition of NaCl, there is a systematic reduction in the cloud point with an increase in NaCl concentration. Also, the cloud point shows a reduction with an increase in PEO concentration from 1% to 5%. The results for PEO 20000 showed lower cloud point values when compared with the values obtained with PEO 4000. However, the results for inulin (Figure 12) showed no cloud point up to 4 mol dm$^{-3}$ NaCl, indicating an absence of dehydration by this electrolyte. With MgSIO$_4$, a cloud point could only be measured at 1.5 and 2 mol dm$^{-3}$ MgSO$_4$, reaching values below room temperature.

Generally speaking, the cloud point is related to the χ parameter. When χ is < 1/2, the chains should remain solvated by the molecules of the medium and the solution is clear; when χ > 1/2, dehydration of the chains will occur and chain–chain interaction takes



**Figure 11.** Cloud points of PEO 20000 at various NaCl concentrations as a function of PEO concentration.
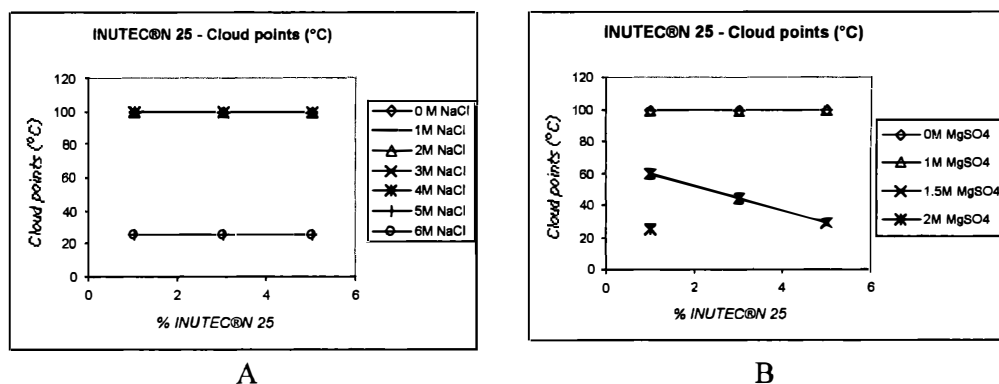
**Figure** 12. Cloud points of INUTEC● N25 at various NaCl (A) and $MgSO_4$ (B) concentrations as a function of INUTEC® N25 concentrations.

place resulting in cloudiness. The cloud point depends both on polymer concentration as well as the molecular weight; with increase in molecular weight and concentration, the cloud point generally decreases, and this can be illustrated from the results shown in Figures 10 and 11. With PEO at 2 mol $dm^{-3}$ NaCl, the cloud point is about 60°C, and if the polymer concentration will reach, for example, 20%, the cloud point could be lower than 50°C. Thus, for emulsion stabilizers based on PEO, stability cannot be maintained at 2 mol $dm^{-3}$ NaCl. With $MgSO_4$, the situation is even worse, as shown in Figure 10: at 5% PEO 4000, the cloud point is lower than RT at 1 mol $dm^{-3}$, and hence instability will be more serious with this electrolyte. However, for inulin the cloud point can be maintained at about 100°C up to 4 mol $dm^{-3}$ NaCl, and hence one would expect stable emulsions at temperatures exceeding 50°C up to this electrolyte concentration. With $MgSO_4$ stability can be maintained at high temperatures up to 1 mol $dm^{-3}$. Thus, these cloud-point measurements give conclusive evidence of the unique behavior of polymeric surfactants based on inulin. The polyfructose chain remains hydrated up to high temperatures and in the presence of high electrolyte concentrations. This makes this polymeric surfactant a very useful candidate for the stabilization of emulsions in high electrolyte concentrations when compared with emulsions prepared using polymeric surfactants based on PEO.

Similar results were also obtained when using cyclomethicone as the oil: 50/50 O/W emulsions prepared using 2 (w/v)% INUTEC® surfactant showed stability at RT and 50°C for more than one year. Emulsions prepared in the presence of 1 mol $dm^{-3}$ NaCl and $MgSO_4$ were also stable up to 50°C for more than eight months.

From the above discussion, it is clear that using HMI as an emulsion stabilizer will eliminate any strong flocculation or coalescence of the emulsion both in water and in high electrolyte concentrations. This can be attributed to a number of effects: (i) the multipoint attachment of the polymer by the several alkyl chains that are grafted on the backbone, ensuring strong adsorption ("anchoring") at the O/W interface; (ii) strong hydration of the polyfructose "loops" (in between the alkyl chains) that dangle in solution, ensuring a $\chi < 0.5$ both in water and high electrolyte concentrations; (iii) high-volume fraction (concentration) of the loops at the interface, recent results using polystyrene latex dispersions (11) showing an adsorbed-layer thickness in the region of

4 nm (and, therefore, the concentration of the polyfructose in this layer is high and this increases the free energy ox mixing according to equation 2); and (iv) enhanced steric stabilization as suggested by Napper (8) for polymers with multi-attachment points.

The hydrophobically modified inulin surfactant can also stabilize the emulsions against Ostwald ripening. The latter arises from the difference in solubility between the small and large droplets. During storage, oil molecules will diffuse from the smaller droplets (which have higher solubility due to their higher curvature) to the larger droplets (with lower solubility due to the smaller curvature). This process can be prevented by using polymers that adsorb very strongly at the O/W interface. As discussed by Walstra (12), this strong adsorption results in an increase in dilatational elasticity, thus reducing the process of diffusion from the small to the large droplets.

## W/O EMULSIONS STABILIZED WITH PHS-PEO-PHS BLOCK POLYMER

W/O emulsions (with the oil being Isopar M) can be prepared using PHS-PEO-PHS block copolymer at a very high water volume fraction (>0.7). These emulsions have a narrow droplet size distribution, with an average radius, R, of 183 nm. They also remain fluid up to high-volume fraction (>0.6), as is illustrated in Figure 13, which shows the viscosity-volume fraction curves for the emulsion (13). The effective volume fraction, $\varphi_{eff}$, was calculated from the relative viscosity, $\eta_r$, using the Douherty-Krieger equation (14):
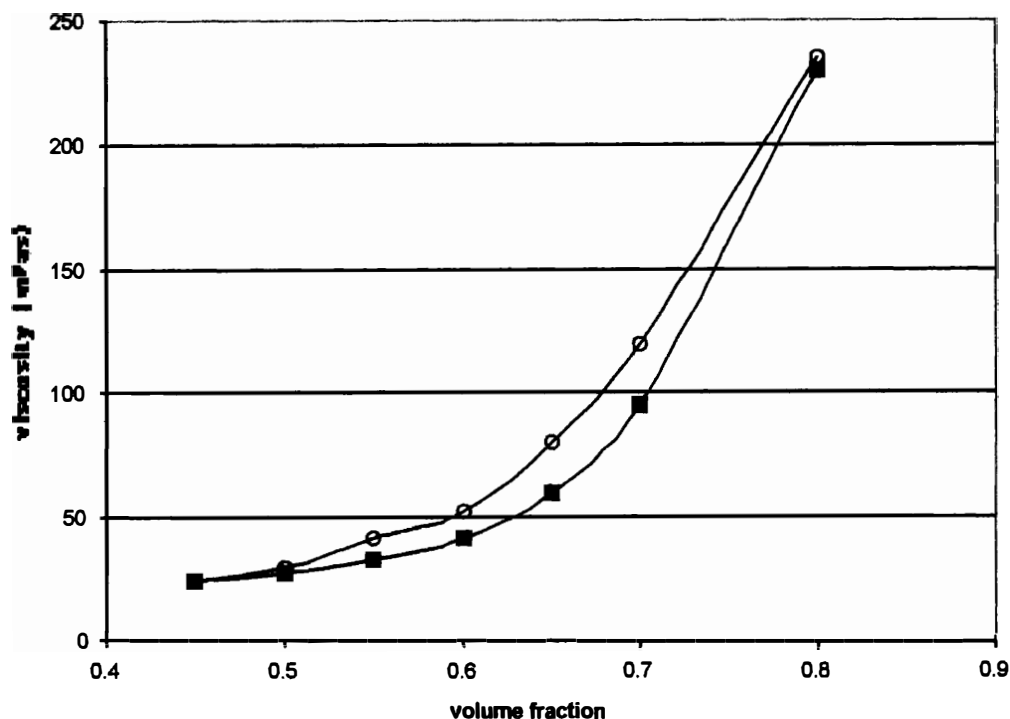


Figure 13. Viscosity-volume fraction curves for W/O emulsions stabilized with PHS-PEO-PHS block copolymer. o, experimental points; ■, calculated using equation 4.

$$\eta_r = \left[ 1 - \left( \frac{\phi_{eff}}{\phi_P} \right) \right]^{-[\eta]\phi_P} \tag{4}$$

where $[\eta]$ is the intrinsic viscosity that is equal to 2.5 for hard-spheres and $\phi_P$ is the maximum packing fraction that was found to be 0.84 (which is a reasonable value for a polydisperse system).

From $\phi_{eff}$ and $\phi$, the adsorbed layer thickness, $\delta$, was calculated using equation 5:

$$\phi_{eff} = \phi \left[ 1 + \left( \frac{\delta}{R} \right) \right]^3 \tag{5}$$

where $\delta$ was found to be ~10 nm at $\phi = 0.4$ and decreased with an increase in $\phi$ as a result of the possible interpenetration and/or compression of the PHS chains.

The emulsions remained stable both at room temperature and 50°C for several months, and there was no evidence of flocculation and/or coalescence, as assessed by using rheological measurements for concentrated W/O emulsions. This stability is expected since the anchor chain (PEO) is soluble in water and insoluble in oil, thus ensuring lack of displacement of the polymer molecules. The PHS chains remained strongly solvated by the oil molecules both at room temperature and at 50°C, and this ensured effective steric stabilization.

## CONTROL OF CREAMING OR SEDIMENTATION OF EMULSIONS

Creaming or sedimentation can be controlled by addition of "thickeners" in the continuous phase. Most of these thickeners are high-molecular-weight polymers such as hydroxyethyl cellulose (or its hydrophobically modified version, referred to as associative thickeners), xanthan gum, alginates, carbomers (e.g., Carbopol), etc. All these materials produce non-Newtonian systems above a critical concentration. This non-Newtonian behavior can be expressed from plots of shear stress, $\sigma$ (Pa), as a function of shear rate, $\dot{\gamma}$ (s$^{-1}$), as is illustrated in Figure 14, referred to as psudopolastic flow.
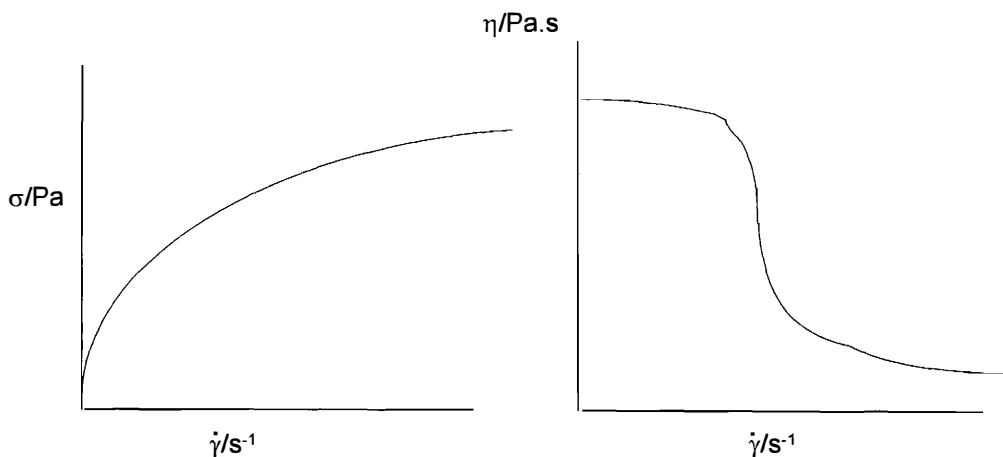


Figure 14. Shear stress and viscosity as a function of shear rate for a psudoplastic system.

As discussed before (15), these systems produce high viscosities at very low shear rates or shear stresses (>100 Pas), and this prevents any creaming or sedimentation of the emulsion.

Another problem with many emulsion systems that are weakly flocculated or "structured" to reduce creaming or sedimentation is "syneresis." The "gel network" produced in the system may contract with time (as a result of gravity forces) and some supernatant liquid may be "squeezed out," leaving a clear liquid layer at the top or bottom of the container. To prevent syneresis, one has to optimize the bulk modulus (which is related to the elastic or storage modulus). The latter can be measured using dynamic or oscillatory techniques that have been described previously (15).

## CONTROL OF PHASE INVERSION

Phase inversion can be of two types: (i) Catastrophic inversion caused by increasing the disperse phase volume fraction above a critical value (mostly above the maximum packing fraction) and (ii) transitional phase inversion produced by changing the conditions, e.g., an increase in temperature with emulsions stabilized by ethoxylated surfactants. Catastrophic phase inversion can be eliminated by reducing the phase volume of the disperse phase in the emulsion. This is usually not a problem since most emulsion systems are prepared at disperse volume fractions well below the maximum packing fraction. Transitional phase inversion has to be prevented by the proper choice of emulsifier. This problem has been discussed in detail by Shinoda and Saito (16). With O/W emulsions based on ethoxylated surfactants, phase inversion may take place at a critical temperature (referred to as the phase inversion temperature, PIT). With increasing temperature, the polyethylene oxide (PEO) chain becomes dehydrated (as a result of the breakdown of the hydrogen bond between EO and $H_2O$). This results in reduction of the aqueous solubility of the surfactant, and at the PIT the surfactant becomes more oil-soluble and hence suitable for formation of a W/O emulsion.

The above-mentioned problem of phase inversion is eliminated when using polymeric surfactants such as hydrophobically modified inulin (HMI). This polymeric surfactant is not oil-soluble at any temperature, and hence by increasing the temperature there is no chance of inversion to a W/O emulsion. As long as no coalescence or Ostwald ripening occurs (as discussed above), the O/W emulsion remains stable up to high temperatures without any phase inversion occurring.

## CONCLUSIONS

This overview shows the main advantages of polymeric surfactants in the stabilization of emulsions for personal care applications. For O/W emulsions, a hydrophobically modified inulin (HMI) graft copolymer is shown to be very effective for stabilization of the emulsions both in water and in high electrolyte concentrations at high temperatures. This is attributed to the multipoint anchor of the HMI at the O/W interface. The loops of polyfructose remain hydrated both in water and in high electrolyte solutions up to high temperatures. For W/O emulsions, an A-B-A block copolymer was the most suitable. A is poly(ethylene oxide) (PEO) (the anchor chain in water droplets), and B is polyhydroxystaric acid (PHS) (the stabilizing chains that are strongly solvated by hy-

drocarbon molecules). Any creaming or sedimentation of the emulsions can be prevented by using "thickeners" (such as hydroxyethyl cellulose or xanthan gum) that produce high viscosity (>1000 Pas) at low shear stresses or shear rates. The HMI polymeric surfactant also prevents phase inversion, since the molecule is insoluble in oil at all temperatures.

## ACKNOWLEDGMENT

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