

Phase Inversion of Polyacrylamide-Based Inverse-Emulsions: Influence of Inverting-Surfactant Type and Concentration

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ABSTRACT: The phase inversion of polymeric water-in-oil emulsions has been systematically studied by employing nonylphenol and alcohol ethoxylates with various chemistries as well as physical chemical characteristics. A combination of thermodynamics, phase diagrams, and rheometry were used to investigate the behavior of the inverting surfactants as well as the inverted, acrylamide-based, cationic emulsions. Polymeric inverse-emulsions containing the inverting surfactant showed no evidence of low-shear thinning, though they did thin as hydrodynamic forces increased (0.01 to 100 s^{-1}) prior to reaching a chemistry- and concentration-independent plateau, as is typical for emulsions. The viscosity of emulsions containing inverting surfactants reached a minimum at 1.2% of the "emulsion breaker". The efficiency of inversion was optimized at 2 wt % of nonylphenols, expressed as a percentage of the total emulsion mass, and increased with the degree of ethoxylation. Interestingly, the viscosity of the polymer inverted in water was maximized at an inverting-surfactant level corresponding to the

CMC of the pure surfactant in water. The alcohol ethoxylates required a higher concentration for inversion (3 wt %), though they provided a higher ultimate inverse viscosity of the polymeric emulsion in water. Therefore, while the inversion process was less efficient with alcohol ethoxylates, the ultimate dilution solution properties of the polyelectrolytes liberated were improved relative to the nonylphenols. Overall, the process of adding a water-in-oil emulsion, containing an emulsion breaker, to an excess of water involves a catastrophic inversion mechanism. To be effective under such circumstances, an inverting surfactant should have a partition coefficient between the aqueous and organic phases greatly exceeding unity as well as a hydrophilic-lipophilic balance (HLB) above 12. Effectiveness increases linearly with the partition coefficient. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3567–3584, 2007

Key words: acrylamide; alcohol ethoxylates; HLB; inverting surfactant; suspension polymerization

INTRODUCTION

Polymeric inverse-emulsions are employed in solid-liquid separations and pushing fluids for enhanced oil recovery. They also find utility in a crosslinked form, as rheology modifiers for cosmetic gels and biotechnology for encapsulation, as well as in targeted drug delivery. For example, polyelectrolytes based on acrylamide copolymerized with cationic comonomers such as quaternized dimethylaminoethyl acrylate are used in the paper sector as formation and retention aids, as well as in municipal or industrial sludge dewatering. Anionic inverse-emulsion copolymers, generally based on sodium acrylate, are employed in the processing of alumina as well as in mining. Polymer coil charge density has recently been proposed as a key variable in understanding the mechanism of interactions between polyelectrolytes and oppositely

charged colloids.¹ Therefore, polymers with between one and three long chain branches per macromolecule are now commonplace, as they can provide higher molar masses and reduced coil dimensions in aqueous solution.

Inverse-emulsion laticies are generally 100 nm to several μm in size. The ultimate form of the inverse-emulsion is dispersion in an organic phase (generally paraffinic). Inverse-emulsions are typically sterically stabilized with a nonionic surfactant blend so as to provide a relatively condensed interface. They offer several advantages to more conventional bulk (or solution) processes, including higher polymer concentrations in the ultimate product. Inverse lattices can also be rapidly dissolved in water, provided a high hydrophilic-lipophilic balance (HLB) wetting agent is mixed into the emulsion post polymerization. Interestingly, although inverse-emulsion polymerization is a commonly used technology to produce high-molecular-weight water-soluble polymers,² the inversion process and the role of such wetting agents have been very minimally investigated and a scientific basis for inversion is lacking.

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Inversion

Emulsion inversion applied to basic water-in-oil or oil-in-water type emulsions has been widely studied by Salager,^{3–5} Brooks,^{6–8} and Dickinson.^{9,10} Phase inversion in emulsions was divided into two different mechanisms, depending upon the path of inversion: transitional inversion and catastrophic inversion.³ Transitional inversion is induced by changing factors that affect the distribution of the emulsifier between the two phases such as temperature, the HLB of the emulsifier, the salinity of the aqueous phase, as well as the polarity of the organic phase. Catastrophic inversion is induced by increasing the fraction of the dispersed phase and has the characteristics of a catastrophe. In this case, a catastrophe implies a sudden change in the behavior of a system, as a result of gradually changing conditions.

Vaessen et al.¹¹ distinguished two mechanisms for catastrophic inversion, which depend on the direction of the phase inversion process:

- When the surfactant is predominantly present in the dispersed phase, the rate of coalescence is high and rapid phase inversion occurs at relatively low volume fractions;
- When the surfactant is predominantly present in the continuous phase, the coalescence rate is drastically lowered owing to the Marangoni–Gibbs effect. At this stage, inversion will not take place until high volume fraction is reached. Experimentally, such a difficult inversion was not detected up to 97% dispersed phase volume fraction.¹¹

Inversion chemistry

The ability to invert a polymer-emulsion with excess water to yield a highly viscous dilute polymer solution (1 Pa s for a 0.1% solution) may be achieved through the use of a wetting agent, also referred to as an “inverting” surfactant or an emulsion breaker (EB). Typical inverting surfactants are ethoxylated alkylphenols, ethoxylated fatty alcohols, or ethoxylated fatty acids, with HLBs between 10 and 14, which are added at 1% of the total post-polymerization mass. Alternatively, a polymeric emulsion can be added to an excess water in the absence of inverting agents, though with inversion effectuated by modifying the water hardness.¹³ This can be controlled by changing the salinity of the water, for example, by varying the concentration of sodium chloride. It is thought that salinity may affect lipophilicity (hydrophilicity) by modifying the surfactant–solvent affinity⁵ and thus the inversion efficiency.

The inversion process may be further influenced by controlling the hydrodynamics of mixing of the polymer-emulsion with excess water containing an inverting agent.¹⁴ The polymer emulsion contacted with water is pumped at high pressure through a static

mixer, such that the flow conditions are turbulent. The presence of eddies arriving at an element of interface is felt during a time τ_k (Kolmogorov time scale). During this time, an amount of kinetic energy per unit mass can be supplied to that element. As the amount of energy supplied exceeds the height of the energy barrier, the system may jump over it and reach the oil-in-water emulsion state.^{10,15}

The aforementioned examples show that there are a variety of approaches for the inversion process, the selection of which depends on the final application. In the present investigation, we have focused on the chemical aspects of inversion and more particularly on the effect played by inverting surfactants. The inversion process was studied with respect to inverting-surfactant type as well as concentration. The following section presents theoretical concepts, in particular, those related to the surfactant-affinity difference (SAD) and formulation–compositions maps so as to assist in the interpretation of the results.

A summary of the theoretical concepts required to understand emulsions and couple the thermodynamics of inversion to the phase mapping of this process^{16–22} is presented in the Appendix.

EXPERIMENTAL

Materials

White crystals of acrylamide monomer (AAM) were purchased from Cytec (Rotterdam, the Netherlands) and used as received. The dimethylaminomethyl methacrylate (DMAEA) quaternized with methyl chloride was obtained from Ciba Specialty Chemicals (Bradford, England) as an aqueous solution (80%). For the polymerization in inverse-emulsion, the aqueous phase was emulsified in Isopar-M, a narrow cut of an isoparaffinic mixture, or Exxsol D-100 (supplied by Exxon Chemical, Köln, Germany). Hypemer HB239 (a linear ABA-type block copolymer of polyester-polyethylene oxide-polyester prepared by reacting condensed 12-hydroxystearic acid with polyoxyethylene), sorbitan sesquioleate (Arlacel 83), polyoxyethylene sorbitol hexaoleate (Atlas G-I086), gifts from Uniquema (Brussels, Belgium), were used as nonionic stabilizers without any purification. Sorbitan monoisostearate (Montane 70) as well as (20)-polyethoxylated sorbitan monooleate (Montanox 80) purchased from Seppic (Paris, France) were also used as nonionic stabilizing agents. Type I reagent grade water with a resistance of 18.2 m Ω -cm was obtained through a series of deionization and organic scavenger cartridges (Milli-Q Synthesis, Millipore AG, Volketswil, Switzerland). 2,2'-azobis(2,4 dimethylvaleronitrile) (V-65, Wako Chemical, Germany) was used as received as oil-soluble initiator.

Certified ACS EDTA (ethylene diamine tetra-acetic acid, disodium salt dihydrate) (Fluka, Switzerland)

was used as a chelating agent in the copolymerization with unpurified monomers. Adipic acid purchased from Riedel-de Haen (Seelze, Germany) was further used to prevent polymer hydrolysis. Nonylphenol with 6-, 8- and 10-ethoxylated units (NP-6, NP-8, and NP-10) and alcohol alkoxyate (Atpol I-731, Atpol I-3531), gifts from Uniquema (Brussels, Belgium), were employed as inverting surfactants to invert the polymer-emulsions with excess water to yield a highly viscous dilute polymer solution.

Polymer synthesis

The polymerization reaction of acrylamide with dimethylaminoethyl acrylate quaternized methyl chloride, whose composition was 73 : 27 mol %, was performed in a 25 L stainless-steel reactor equipped with a heating/cooling coil. The water-to-organic phase ratio was 2.6 : 1 by weight. The monomer concentration was 40 wt % of the total mass of emulsion and the emulsifier blend was dissolved in the organic phase at a concentration of 2.3 wt % of the total reaction mass. The HLB value was approximately 5.8. The chemical initiator 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65, Wako Chemicals, Neuss, Germany) dissolved into xylene was added into the reactor at 40°C. The reaction time was 6 h and the temperature of reaction was further increased, stepwise, up to 52°C in order to initiate the polymerization.

Inversion and viscometric characterization of the inverse-emulsion

The inversion of polymerized inverse-emulsions was carried out as follows. In a large and baffled beaker (1 L capacity), 300 g of deionized water was stirred at 400 rpm (Rushton type of impeller). A precalculated amount of emulsion (containing the inverting surfactant) was added to yield 0.1 wt % active weight of polymer in solution. This injection was carried out within a short time (less than 1 sec) directly to the center of the vortex. The agitation speed was further increased to 600 rpm and maintained for an additional 5 min. A rapid increase in solution viscosity and the absence of agglomerates in the aqueous phase usually indicated a good inversion. The resulting polymer diluted solution was then characterized by viscosity measurements. The polymer viscosity was measured with a model L VDVII+ viscometer (Brookfield, Stoughton, MA) at 50 rpm and room temperature.

Static interfacial tension

The interfacial tension as function of the concentration of the inverting surfactant in the model system was measured at room temperature (20°C) using the Du Nouy ring method [28] with a KSV Sigma 7⁰³ tensi-

ometer (KSV Instr. LTD, Helsinki, Finland). The interfacial tension thusly measured was found to be reproducible within 1.0 mN/m.

The inverting surfactants were initially dissolved in the aqueous phase. Then the ring was lowered on the surface of the aqueous phase, such that it was wetted completely by the liquid. Finally, the organic phase was carefully added (along the walls of the beaker) on the top of the aqueous phase, such that a model interface was created. For simplicity and sensitivity of the measurements, it was decided not to consider stabilizing agents in the model interface (emulsion). The measurement started as the ring was pulled out of the aqueous phase and the upper side of the ring was touching the interface; the force started to increase continuously until a maximum was reached. At this point, the volume of liquid pulled up by the ring was also at its maximum. The maximum equilibrated force required to detach the circular ring from the interface was the interfacial tension measured.

Partitioning studies

A set of partitioning studies were performed to determine the equilibrium partition coefficient of the inverting surfactants between the organic and aqueous phases. The organic phase consisted of a 0.01 grnL⁻¹ inverting-surfactant solution prepared with paraffinic oil, while the aqueous phase consisted of highly deionized water. Dispersions were prepared using an organic-to-aqueous phase ratio of 1 : 1 (volume). The dispersions were agitated vigorously for one hour by mean of a vortex mixer (Maxi-Mix III, Wohlen, Switzerland). The phases were then decanted for periods of up to 24 h. The transparent organic phase (upper layer) was carefully taken off and its UV absorbance was determined. The UV system was a Lambda 18 Model from Perkin Elmer (Beaconsfield, England) and all measurements were carried out at 290 nm. The concentration of the dissolved inverting agent in the paraffinic oil was then estimated from a calibration curve representing the intensity of absorbance as a function of concentration. By knowing the concentration of the breaker in the oil phase, the concentration of the inverting surfactant in the aqueous phase was determined from the initial concentration. Accordingly, the partition coefficient (K_p) is expressed as follows:

$$EB_{\text{organic}} \Leftrightarrow EB_{\text{aqueous}} \Rightarrow K_p = \frac{C_{EB,\text{Aqueous}}}{C_{EB,\text{Organic}}} \quad (1)$$

A calibration curve (referred to as "EB", which designates an emulsion breaker) was obtained for each inverting surfactant by measuring the UV absorbance (at 290 nm) of a series of concentrations of EBs dissolved in paraffinic oil. The concentration prepared

TABLE I
Specifications of the Surfactants Employed in this Study

| Inverting-surfactant name | Chemical structure | Degree of ethoxylation | HLB | Solubility | Partition coefficient | Interfacial activity at the W/O interface (mN/m) | CMC (g/mL) |
|---------------------------|-------------------------|------------------------|------|----------------------------------|-----------------------|--------------------------------------------------|---------------------|
| NP-10 | Ethoxylated nonylphenol | 10 | 13.3 | Water, vegetable oil, ethanol | 3.9 | 4.98 | $5.5 \cdot 10^{-5}$ |
| Ethylan TU | Ethoxylated nonylphenol | 8 | 12.3 | Water | 3.0 | 4.84 | $5.5 \cdot 10^{-5}$ |
| NP-6 | Ethoxylated nonylphenol | 6 | 10.9 | Kerosene, vegetable oil, ethanol | 1.2 | 4.66 | $5.5 \cdot 10^{-5}$ |
| Atpol I-731 | Alcohol rthoxylate | No data | 10.9 | Water | — | 4.26 | $1 \cdot 10^{-5}$ |
| Atpol I-3531 | Alcohol rthoxylate | No data | 10.2 | Water | — | 3.76 | $1 \cdot 10^{-5}$ |

ranged from 0.001 g mL^{-1} to 0.008 g mL^{-1} . This method worked very well for the nonylphenols and was inappropriate for the alcohol ethoxylates.

Evaluation of the consistency of diluted polymer solution

The consistency, which describes the state of organization of the fluid, was used as a metric to characterize the final diluted polymer solution. To evaluate the consistency of the mixture, we carried out a simple straining test, which allows one to distinguish between viscouslike and viscoelasticlike behaviors. A rod is initially plunged into the polymer solution, and then the mixture behavior is evaluated as the rod is suddenly taken off the solution. Two situations are observed. When long a thin thread follows the stick as soon it goes out of the solution; this is referred to as a viscoelasticlike behavior. In contrast, when the liquid mixture does not stand close to the stick, such that no material leaves the beaker, it referred to as a viscouslike behavior.

RESULTS AND DISCUSSION

Physical chemical characterization of the inverting surfactants

Five inverting surfactants with similar molecular weights, different degrees of ethoxylation as well as two chemical structures were used to investigate the emulsion inversion process. The amounts of ethoxylation were varied such that the HLBs could be systematically examined. The characteristics of the five species are presented in Table I. Partition coefficients of nonylphenol ethoxylate-type inverting surfactants are also shown. It is evident that the inverting surfactant with the largest number of ethoxylation units presents the highest affinity to water. The critical micelle concentrations of the various inverting surfactants were also evaluated. Since CMC depends almost entirely on

the nature of the hydrophobic moiety on the surfactant, it seems obvious that the reported CMC for the two different chemistries of inverting surfactants differ. Moreover, within a family, the hydrophobic moiety is unchanged and the CMC is therefore insensitive to, for example, the degree of ethoxylation on the hydrophilic head of the surfactant, as would be expected. Table I also demonstrates that the interfacial tension follows the HLB values, regardless of the chemical structure of the inverting surfactant. From these observations, it is relatively clear that the ethoxyl unit is interfacially active, and partition coefficients alone cannot characterize the effect of the inverting surfactant on destabilizing the inverse-emulsion, as was also noted by Kim.²³ In other words, a destabilizing species having a high partition coefficient may not suppress the interfacial gradient of the film emulsion if the components of the destabilizing agent are not interfacially active.

Rheological characterization of polymer W/O emulsions containing inverting surfactants

Typical examples of the steady shear viscosity of inverse-emulsions of an acrylamide and DMAEA copolymer containing inverting surfactants are shown in Figure 1. Both curves present similar characteristics, with the absence of a low-shear-viscosity plateau, followed by a shear thinning region and then the onset of a high-shear-viscosity plateau. This qualitative behavior of the flow curves appears to be typical for suspensions consisting of colloidal particles that interact repulsively due to their steric stabilization,²⁴ despite the inaccessibility of a low-shear-viscosity plateau. Papir et al.²⁵ and Otsubo et al.²⁶ obtained viscosity curves with similar shape, that is, a shear thinning zone followed by a Newtonian plateau region.

The dominant interactions, which control the rheological behavior of hard-sphere suspensions, are droplet-droplet interaction forces, Brownian forces, and

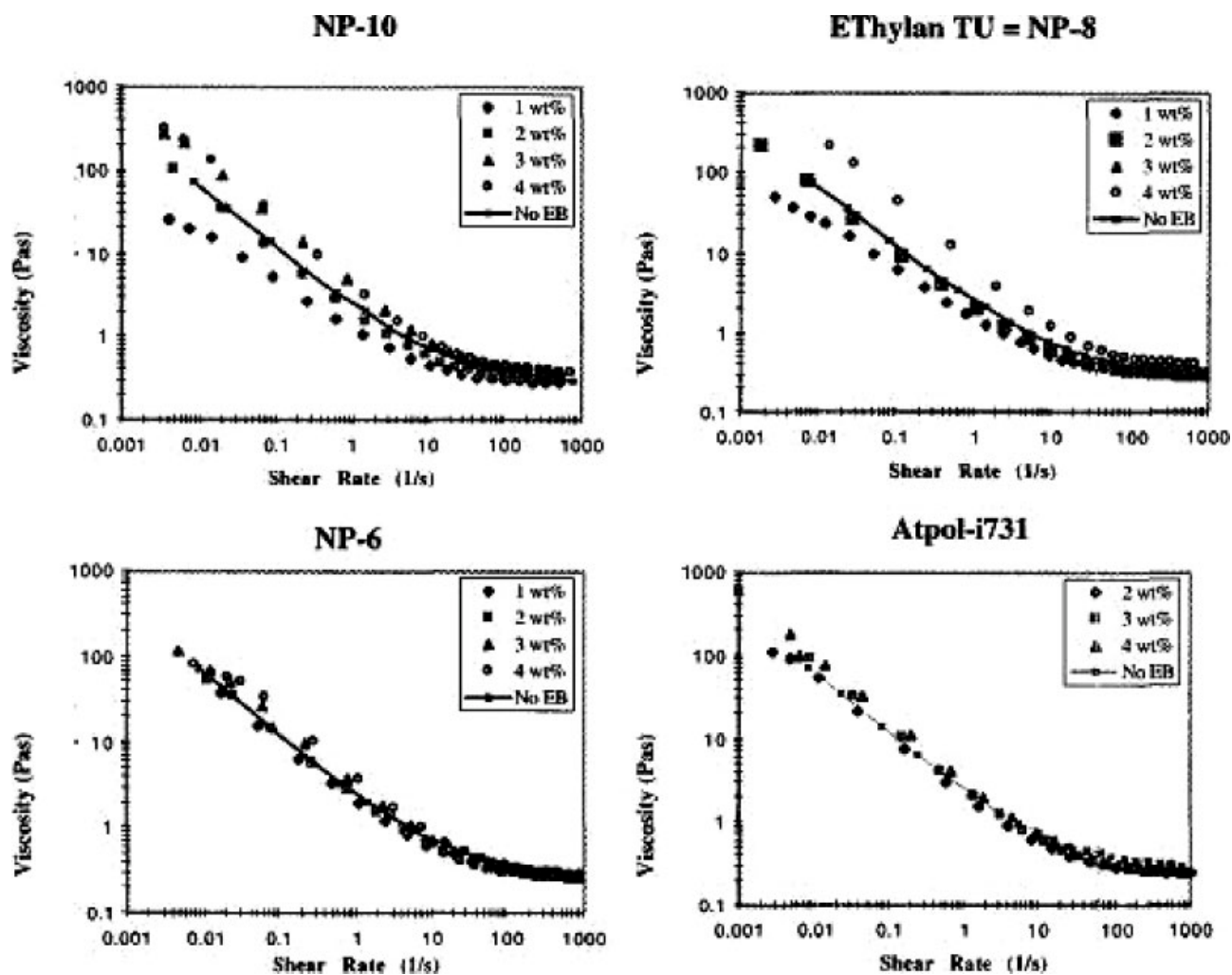


Figure 1 Viscosity profile of polymeric inverse-emulsions containing inverting surfactants. The four panels illustrate the influence of emulsion breaker chemistry and concentration. The solid line represents the polymeric inverse-emulsion in the absence of inverting surfactants. Experimental conditions: temperature ($22 \pm 2^\circ\text{C}$); agitation speed (500 RPM); time of addition (30 min).

hydrodynamic forces.²⁴ The low-shear Newtonian plateau would represent the equilibrium, or zero-shear structure, of the dispersion under Brownian forces and interparticle potentials provided that two conditions are met. The polymerized droplets would have to be equivalent to hard spheres; this seems reasonable since the internal phase viscosity is very high compared to the continuous phase, and the particle radius-to-layer thickness ratio is very high. Furthermore, the zero-shear viscosity is out of the range of the applied shear stress. As shear is increased beyond this low-shear plateau, hydrodynamic forces come into play, and the system progressively transforms itself into a structure of ordered sheets of particles parallel to the flow planes, which result from aggregates and interaction rupture. The shear thinning may be compared to a transition regime. At higher shear, the infinite shear viscosity corresponds to a fully ordered bidimensional structure, and the fluid is again Newtonian.²⁷ From these considera-

tions it is evident that viscosity curves of polymer emulsion containing different EB concentrations reach a similar high shear viscosity, since particles are completely separated and, thus, their interactions are negligible compared to hydrodynamic forces.

The contributions of the inverting surfactants to the rheology of the polymer emulsion are shown in Figure 2. Their viscosities exhibited a shallow minimum at approximately 1.2 ± 0.2 wt % inverting surfactant [for nonylphenol (polyethylene oxide)_n only] and was, further, independent of the type of EB used over the range tested. Woods et al.,²⁸ when studying the effect of surfactants on latex rheology resulting from emulsion polymerization, observed a similar trend. They determined the surfactant level corresponding to 100% monolayer coverage of the particle from surface-tension measurements and, further, prepared lattices with different coverages (80%, 100%, and 120%). According to their observations, lattices

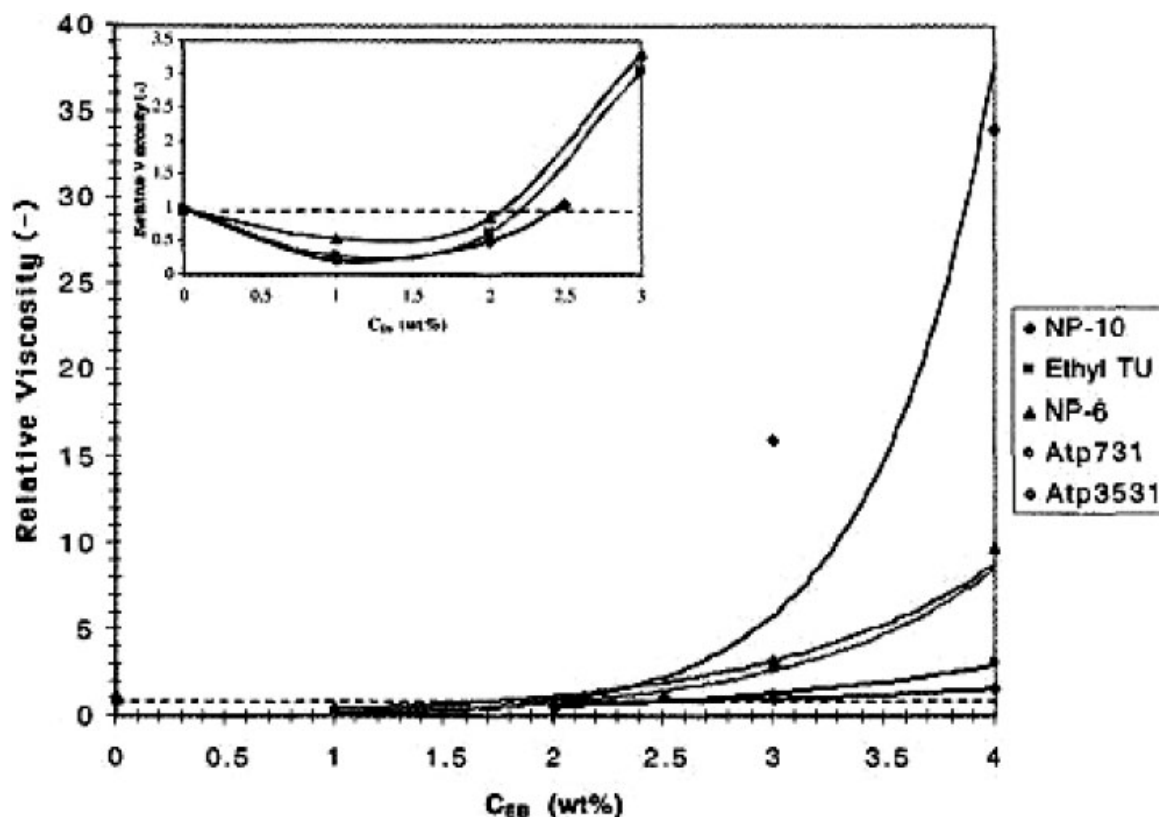


Figure 2 Relative viscosity of polymeric inverse-emulsions as a function of the inverting-surfactant chemistry and concentration. The small chart in the upper left-hand corner depicts the relative viscosity below unity for nonylphenol ethoxylate based inverting surfactants. The relative viscosity was defined as the ratio between the viscosity of the polymeric inverse-emulsion in the containing EB relative to that in the absence of EB.

with 100% surface coverage exhibited the lowest viscosity. Beyond 100% coverage, the viscosity increase was attributed to a possible micellization of the excess surfactant, while the increase below 100% coverage was thought to stem from a tendency toward aggregation. When considering the situation examined in this article, surfactant-stabilized polymer W/O emulsions are subject to some perturbations as the inverting surfactant is added to the system, since the latter has enhanced hydrophilic properties. As a result, we observed viscosity changes from its original state. An attempt to explain such a phenomenon is proposed here and focuses only on nonylphenol ethoxylate agents.

During the first addition step (0 to 1 wt %), the viscosity decrease might be attributed to possible aggregate break-up, which resulted from liberation of the oil phase entrapped within the interstices of the aggregates and, therefore, fluidity was increased. Furthermore, the adsorption of surface active agents should also affect the species distribution at the interface (an interface has no sharply defined boundaries and is rather defined as a region over which the density and local pressure varies,²⁹ such that part of oil molecules comprising the interface were replaced by inverting surfactants. However, we assumed that such a transfer was rather small compared to oil release from the

break-up of aggregates. As the EB concentration was further increased (above 1.2 wt % EB), the emulsion viscosity increased due to micellization or complexation. Measurements of the oil-phase viscosity containing different concentrations of inverting-agents revealed that the best EB were only barely soluble in oil (see partition coefficients data, Table I) and formed either clouds or lenses that settled rapidly at rest (Table II). Hence it is likely that, as postulated, they end up in the volume delineated by the interfacial sheath, prior to inversion, and containing the nonionic surfactants, some of whom are displaced by the EB, and the associated organic phase molecules. Such an "EB film" which is located between hydrophilic polymer droplets may reduce the drainage, and thus the viscosity increases. This hypothesis seems reasonable because, following the EB addition, polymer emulsions were observed to be stable over periods exceeding at least a week, concomitant with a viscosity increase.

To illustrate the aforementioned discussion, a "relative viscosity" — the ratio between polymer emulsion containing EB to polymer emulsion free of EB as a function of inverting-surfactant concentration — is plotted in Figure 2. Relative viscosity below unity was thought to correspond the case where aggregate break-up occurred, while above unity the viscosity

TABLE II
Viscosity Measurements of Organic Phases with Inverting Surfactants

| Property | Inverting surfactant | | | |
|-------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|------------------------------------------------------|----------------------------|
| | NP-10 | Ethylan TU | NP-6 | Atpol I-731 |
| Viscosity of inverting surfactant oil mixture (mPa s) | 1 wt %: 2.5 4 wt %: 2.7 | 1 wt %: 2.7 | 1 wt %: 2.8 4 wt %: 6.6 | 1 wt %: 2.7 4 wt %: 3.5 |
| Appearance | Turbid, separation of phases and settling of heavy phase, formation of small "lenses" | Turbid, separation of phases and settling of heavy phase, formation of small "lenses" | Turbid, separation of phases and settling after 24 h | Turbid and cloudy |

increase was attributed to interface complexation or reorganization of the EB. The exact interpretation of the minimum is still a matter for reflection, since it does not correspond to the optimum inversion point, as discussed below. However, the fact that the optimum in inversion for the nonylphenols corresponds to the crossover point (2 wt %) indicates, as expected, that interfacial disintegration precedes the formation of a novel interface containing EB.

In summarizing the contribution of inverting surfactants to the rheology of the polymer emulsion, it should be noted that the sharpness of the curves were strongly affected by the EB chemistry. The inverting surfactant's affinity for water may be responsible for such behavior, and thus it is evident that an EB with the highest HLB resulted in the highest viscosity, while the opposite was true with the lowest HLB inverting-agent.

Influence of inverting-surfactant chemistry on the inversion efficiency

Nonylphenol-type inverting surfactants

The experimental phase inversion of the polymer-based W/O emulsion as function of concentration for three nonylphenol-type breakers is presented in Figure 3, reported as the viscosities of diluted polymer solutions. As expected, the efficiency of inversion increases with an increase in the degree of ethoxylation of the inverting surfactant. The optimal inversion efficiency of the polymer emulsion was observed for concentrations approaching 2 ± 0.2 wt % inverting surfactant and was further independent of the type of EB used over the range tested. This result is important, since it provides a means of preparing maximized inverted diluted polymer solutions with low concentration of breaker. Furthermore, Figure 3 reveals that the inversion efficiency increases as the concentration of the inverting-agent increases up to a maximum value above which viscosity of the diluted polymer solution decreases. At the optimum concentration, it was thought that breaker surfactants completely covered the water-oil interface, thus favoring the phase-inversion process accompanied by the polymer release into water. As EB was further

added, the viscosity decrease was attributed to a subsequent dissolution of EB in either oil or water, depending on its relative solubility, partition coefficient,³⁰ and HLB. As a result, enhanced emulsion stability was observed because of repulsion forces generated by the layers of surfactant molecules surrounding the droplet surface. This last explanation was proposed by Zaki et al.³¹ when studying demulsification of asphaltene stabilized water-in-benzene emulsion, and was assumed to be valid for our purpose. Goldszal et al.³² attributed this effect to enhancement of lateral interactions with increasing the surfactant concentration, which increased the interfacial film rigidity, and thus reduced the power of destabilization. To complete the presentation of the results, it should be pointed out that phase inversion occurred, even in the absence of EB as depicted in Figure 3. Indeed, a value of 160 mPa was measured, which is far from the viscosity of pure water (1 mPa), describing the case of no inversion at all. We have proposed the following hypothesis to explain such a behavior:

- Phase inversion occurs partially because the stabilized polymer droplets already contain a surfactant with a high HLB. Indeed, the primary water-in-oil emulsion was stabilized by a mixture of surfactants, one of which was (20)-polyethoxylated sorbitan monooleate, whose HLB was approximately 10, and the second one corresponded to sorbitan mono-isostearate having HLB of approximately 3.7. The overall HLB was fixed at 5.8. Therefore, one may assume that the presence of a more hydrophilic surfactant in the mixture promotes inversion. As excess water is in contact with the polymer emulsion, the water-soluble surfactant may transfer to the inner boundary layer where it is thermodynamically more favorable, which results in partial inversion due to an insufficient amount of water-soluble surfactants.
- Following an idea developed by Dickinson,⁹ the stirring of an emulsion may provide energy to the system such that it "jumps" over a certain energy barrier. This barrier depends on the curvature as well as the population at the interface. Therefore, the presence of surfactants at the

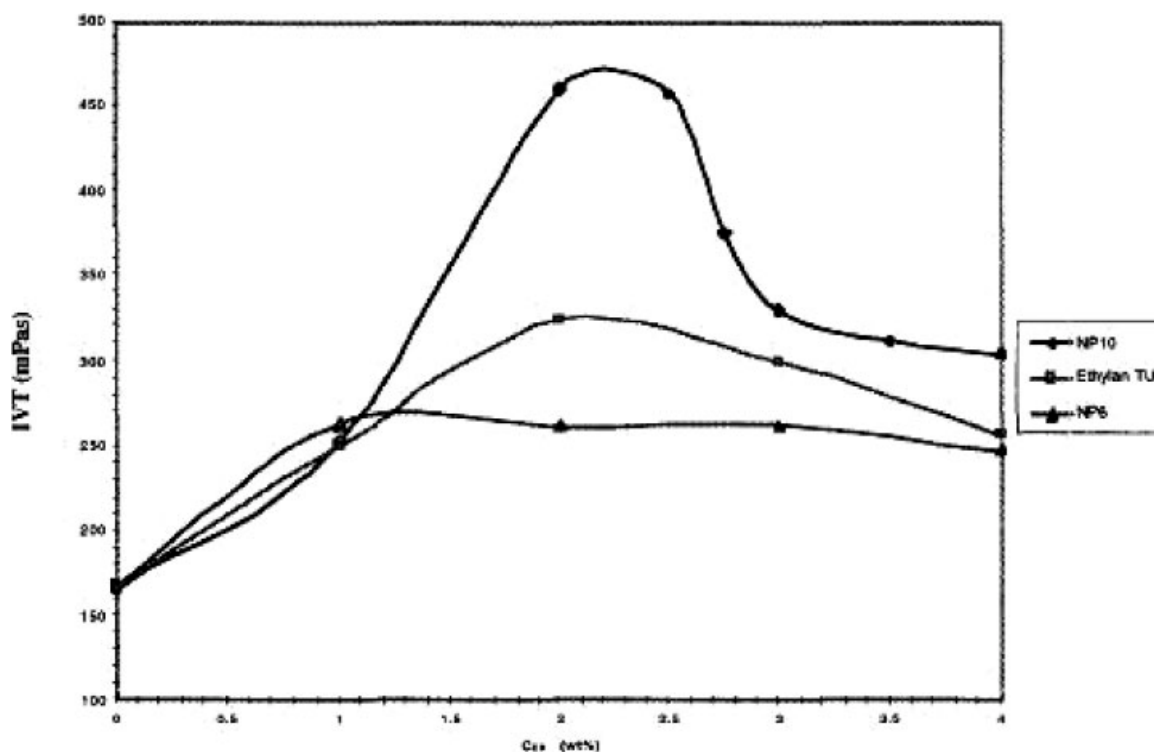


Figure 3 Efficiency of inversion as a function of concentration for three nonylphenol-type inverting surfactants. Viscosity measurement (IVT) was used as a metric to evaluate inversion performance. IVT measurements of diluted polymer solutions were carried out after 5 min of stirring.

interface might reduce the total surface energy to a certain extent so that the energy provided by stirring allows this partial inversions.

The formulation–composition maps mentioned in the introduction will now be applied to understand the behavior of a polymer W/O emulsion in which 2 wt % nonylphenol ethoxylate (with different HLB) is added prior to inversion (Fig. 4). The different EB HLBs confer to the initial polymer emulsion a new “state” whose distance from the optimum formulation may influence the inversion process. As the ethoxylate number on the inverting surfactant is reduced, its distance from the zero surfactant-affinity difference (SAD) point increases. This is mathematically observed by the relationship between the partition coefficient and SAD in eq. (A1), where higher partition coefficients yield lower SADs, as well as the data in Table I, which illustrate that the partition coefficient increases with the EO number. Therefore, one reason that the nonylphenol with a higher number of EO groups is more effective is that it partitions favorably into the aqueous phase. It is possible that the breadth of the intermolecular distribution of EO groups would also be important, though suitable models were not available to test this hypothesis.

As inversion proceeds (that is, as polymer emulsion is added to the excess water), the different formulations give rise to different extents of inversion, due to the physicochemical features of the EB. Specifically, the

higher the HLB of EB and the closer it is to the optimum ($SAD = 0$), then the inversion will take place in the most efficient manner. Furthermore, the change in flow properties occurring during inversion, as a result of polymer dissolution, may affect the final extent of inversion such that it may be incomplete at low HLB. On the contrary, when an EB with 10 ethoxylate groups is used, the amount of excess water necessary to invert the system seems to be far from the inversion line, such that the polymer release happens in more diluted conditions (shaded area in Fig. 4) and, therefore, the extent of the inversion may be higher. Should the latter be true, as is observed in the data shown herein for the nonylphenols, it implies that, as discussed in the introduction, inversion is catastrophic in nature. Furthermore, should the slant in the vertical line in Figure 4 be true, it would indicate that the inversion is not merely dependent on the formulation but also on the composition. To test this hypothesis, a series of inversions will be carried out with a different chemistry from the nonylphenols.

Alkoxylated-type inverting surfactants

Figure 5 shows the experimental data on the phase inversion of polymer emulsion as a function of concentration for two alkoxylate-type inverting surfactants. As expected, the inversion efficiency increased as the concentration of the inverting agents rose up to a maximum

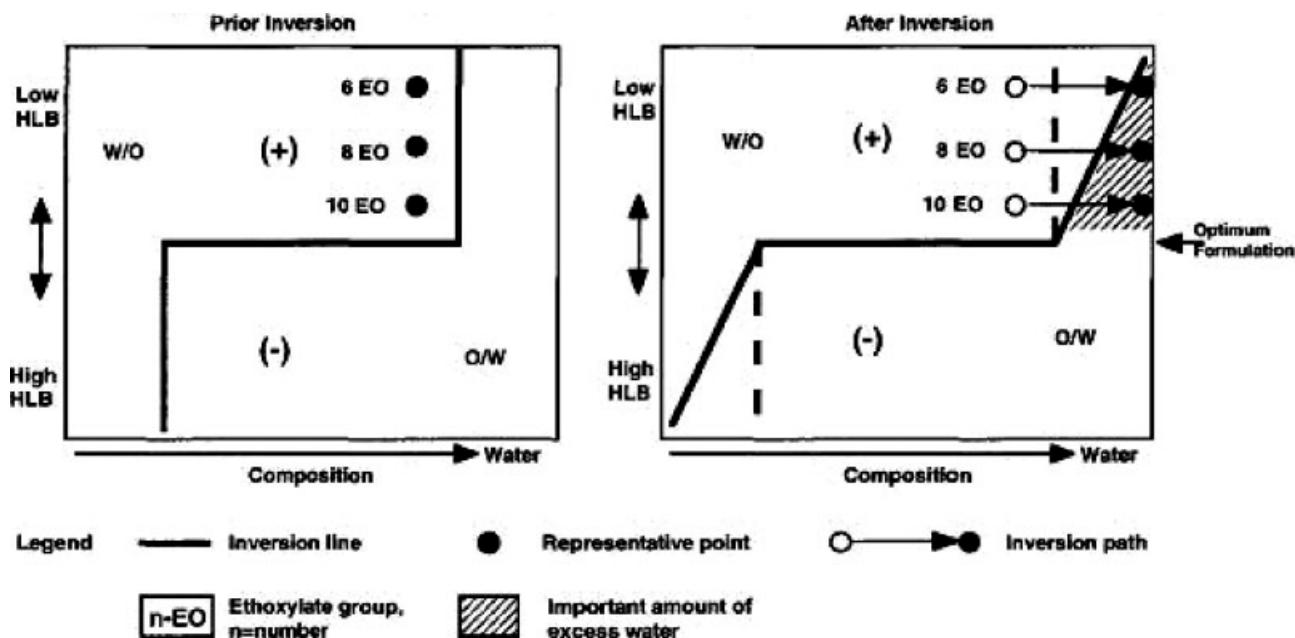


Figure 4 Dynamic inversion patterns of polymeric inverse-emulsions containing nonylphenol ethoxylate inverting surfactants. The region labeled (+) denotes a larger surfactant affinity for oil, while the (-) region implies a preferential affinity for water. Initially, polymeric inverse-emulsions are located in the upper part of the figures, where SAD is greater than zero, since the stabilizing surfactants are oil soluble. As various EBs are added, each with a different HLB, the location of the emulsion in the aqueous region (i.e., the “representative points”) change, as depicted in the panel on the left. This formulation–composition map depicts a specific concentration of surfactant and inverting surfactant. The inversion (in the right panel) illustrates that as the EO number decreases (distance from the SAD is larger), the inversion path is further from the dynamic inversion line, implying a less effective inversion.

value, above which the viscosity of the diluted polymer solution decreased. The optimal inversion efficiency of the polymer emulsion was observed for concentrations equal to 3 ± 0.2 wt % inverting surfactant and was independent of the type of EB used, over the range tested. The same observation was made for phase inversion of polymer emulsion with nonylphenol-type agents (Fig. 4), although the optimum inversion efficiency occurred at a lower concentration (2 ± 0.2 wt %).

Despite the slight shift of the optimum to higher EB concentrations, all comments and observations presented in the previous section remain valid for the inversion of emulsions by means of the alcohol-alkoxy-ate type of inverting agents. However, an attempt to explain this difference will be discussed in a subsequent section. Indeed, it is thought that polymer–surfactant interactions, as well as some physical properties of surfactants in solution, are influencing the final state of the polymer in solution leading to an enhanced viscosity. Furthermore, it is clear that the chemistry has an influence on the inversion and that the slanted nature of the “vertical” line in Figure 4, indicating catastrophic inversion, is borne out.

Influence of structural variations of the inverting surfactants on their inversion efficiency

The selection of an inverting surfactant is often based on the process of trial and error. However, the identifi-

cation of structural variables as well as other physical parameters, such as solubility³¹ and interfacial tension,^{32,33} which influence the inversion performance of an inverting surfactant are also thought to play a major role. An attempt to answer these questions is presented below, based on studying the inversion performance of a series of inverting surfactants having a systematic variation in HLB and architecture type.

Effect of the HLB of the inverting surfactant on the inversion process

The HLB concept, which was first introduced by Griffin,³⁴ finds its importance in predicting the action of stabilizing agents on water-in-oil emulsions. However, this concept, has been rarely used by the scientific community as they were investigating demulsification, Shetty et al.³⁵ have found that a water-soluble wetting agent could effectively destabilize a water-in-oil emulsion. Their study based on the influence of HLB and the molecular weight of the wetting agent showed that a wetting agent could have a very good performance when it contained a high percentage of hydrophilic groups (high HLB) and low molecular weight. Furthermore, Cooper et al.³⁶ and Averyard et al.³⁷ found that the HLB of a system was an important factor for producing effective demulsification. In the present study, the HLB value of the inverting surfactant was varied by changing the degree of ethoxylated units in

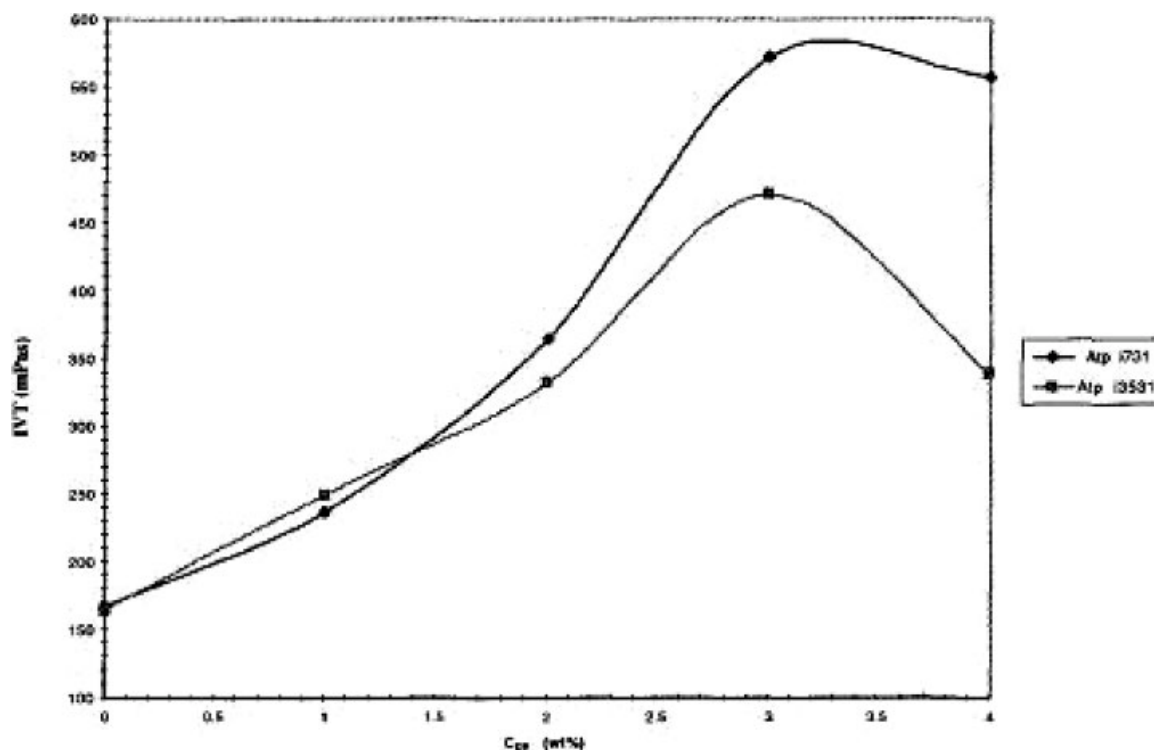


Figure 5 Efficiency of inversion as a function of concentration for two alcohol alkoxyate-type inverting surfactants. IVT measurements of diluted polymer solutions were performed after 5 min of stirring.

a nonylphenol-type EB. In addition a comparison with another EB having different chemical structure will be presented. For the polyethoxylated nonionic surfactants, with no other hydrophilic groups, the HLB was estimated through Griffin's (16) equation as:

$$HLB = \frac{100}{5} \times \frac{W_{OE_n}}{MW_s} \quad (2)$$

where W_{OE_n} accounts for the weight of polyethylene oxide chain and MW_s is the molecular weight of the surfactant. It can be seen from Table I that the HLBs of the surfactants increase with increasing number of ethoxylated units. Interestingly, the same dependence was observed with the partition coefficients values, as discussed below.

The effect of HLB on the viscosity of diluted polymer solutions is shown in Figure 6. In the first case (A), we reported the maximum viscosity achieved with each inverting surfactant, while case (B) presented the data at a unique EB concentration (2 wt %). As expected, the viscosity of the inverted solution increased with increasing HLB of the inverting-agent, over the range tested. The following hypotheses are proposed to explain these findings:

- Increasing the HLB value of the inverting surfactant increases its solubility in the aqueous phase (dispersed phase). From a thermodynamic point of view, as the EB is initially introduced to the

water-in-oil emulsion, it will be more stable at the water-oil interface of the droplet. Accordingly, the concentration of the surfactant at the interface will increase by increasing the HLB value. As the concentration of inverting surfactants increases at the interface, a continuous hydrophilic pathway might be formed between the dispersed droplets and the surrounding excess water. This could result in the rupture of the interfacial film surrounding the water droplets.³⁸

- The enhanced inversion efficiency of the more hydrophilic inverting surfactant may also be explained with the concepts of Laurence et al.³⁹ Destabilization of the water-in-oil emulsions can be achieved by the addition of surface active agents that promote the formation of oil-in-water emulsions. Indeed, it is generally recognized that water-soluble surfactants support stable oil-in-water emulsion formation.⁴⁰ Therefore, since polymer-based water-in-oil emulsions are under investigation, it is obvious that the higher the HLB, the better the inversion.

In their work on demulsification, Cooper et al.³⁶ found that demulsifiers of the ethylene oxide co-propylene oxide type with HLB values ranging between 13 and 15 were considered as the most effective species in breaking water-in-oil emulsions. Although we did not investigate beyond an HLB of 13, the results with the polyethoxylated nonionic surfactants are in

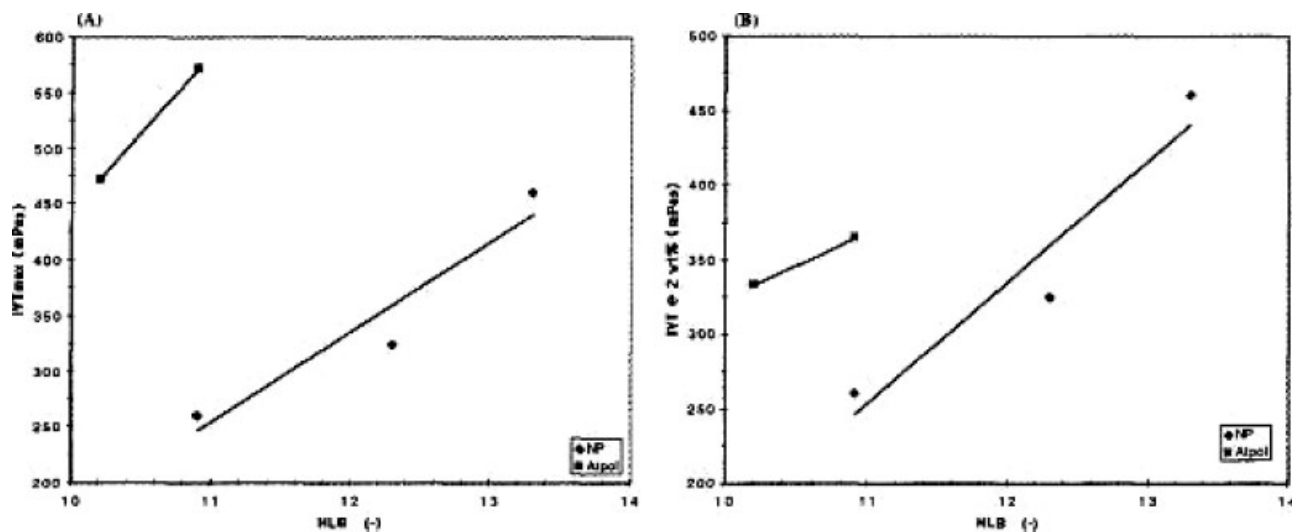


Figure 6 Viscosity of diluted polymer solutions after inversion, and as a function of HLB. The diamond-shaped symbols refer to nonylphenol-type inverting surfactants, while the squares indicate alcohol alkoxylates. Case (A) depicts the maximum viscosity achieved from inversion at optimal EB concentrations (which is a function of the EB chemistry). Case (B) compares the diluted polymer solution viscosities at a single EB concentration (2%).

close agreement to what is found in demulsification. Therefore, it would be interesting to perform further investigations at higher HLB (from 14 up to 20) and see if inversion efficiency reaches an optimum such as observed in demulsification.³⁶

The comparison of the two types of inverting surfactants on inversion efficiency (Fig. 6) shows that emulsions inverted with alcohol ethoxylates have enhanced viscosity, despite the lower HLB values used. Although the optimum EB concentrations required to reach the maximum viscosities were different, depending on whether nonylphenols or alcohol ethoxylates were employed (in the first case the maximum is obtained at 2 ± 0.2 wt %, while in the second case the maximum is reached at 3 ± 0.2 wt % EB), the excess of the alcohol ethoxylate inverting surfactant in the continuous phase cannot by itself explain such a large difference. Indeed, the inverted polymer solution is a complex heterophase system (the water and oil phases are coexisting with a mixture of at least three surfactants) in which different interactions might come into play. Furthermore, these observations should be related to the consistency of the final polymer solution as has already been discussed. Overall, the HLB study supports the data in the previous section (Fig. 4) where the formulation–composition map predicted a chemical role of the inverting surfactant.

At the optimum concentration of inverting surfactant, the structural morphology of the fluid polymer solution was observed to change from viscous-like to gel-like (viscoelastic), for the case of nonylphenols, while the opposite (gel-like to viscous-like) was noted when alcohol ethoxylates were employed. In other words, these maxima might result from different kinds of organization in the polymer fluid phase, which may be

caused by some interactions which depend on the type of inverting surfactants used. As an illustration, Figure 7 depicts the viscosity of diluted polymer solution as a function of concentration for two surfactants with a similar HLB value (HLB = 10.9), though a different chemical structure. Despite their identical hydrophilic-lipophilic properties, a dramatic deviation was observed as the concentration exceeded 2 wt % the alcohol ethoxylate Atpol 1-731, as shown in Figure 7. It may be expected that the difference was the result of a larger amount of polymer dissolved in the water in the case of Atpol 1-731. However, the low interfacial activity and the “low” HLB of the Atpol 1-731 are thought to limit its efficiency for inversion compared to the nonylphenols (the interfacial activity describes the potential of the surfactant to adsorb at the interface). An attempt to explain the reasons behind the chemical role of the inverting surfactants is proposed in the following two sections.

Polymer–surfactant interactions

The interactions of polymer and surfactant are well known to affect the rheology of these mixed solutions.^{41,42} The dominant interactions are hydrogen bonding, electrostatic forces, and hydrophobic interactions. Depending upon the surfactant concentration as well as the polymer type, polymer–surfactant association may be cooperative ($< \text{CMC}$) or noncooperative ($> \text{CMC}$). These are differentiated by whether the polymer bridging and viscosity increase occur at surfactant concentrations well below the CMC of the pure surfactant or occur above the CMC.⁴¹ Furthermore, viscosity curves as function of surfactant concentration showed that the viscosity increased up to a

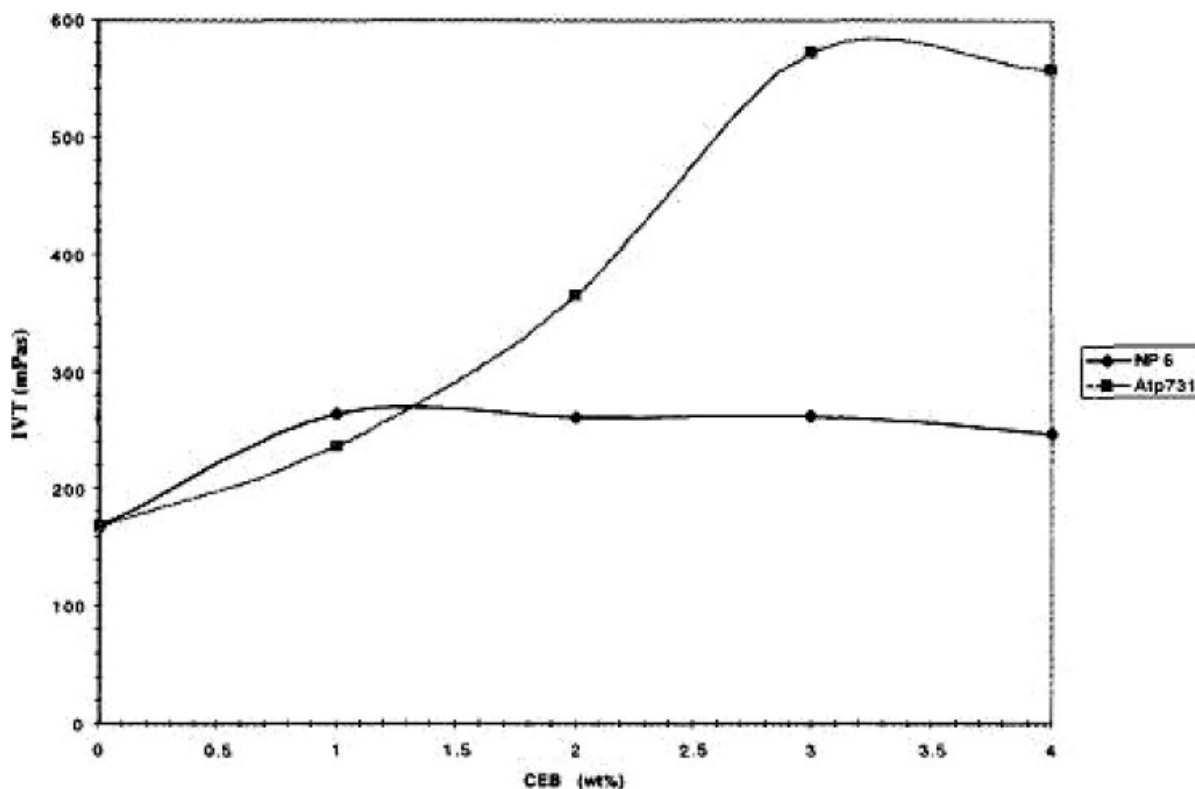


Figure 7 Polymer solution viscosity of the two phase-inversion processes carried out with two inverting-surfactant chemistries, though at an identical HLB of 10.9.

maximum and was then followed by a decrease. The explanation was that surfactant associated with the hydrophobic part of the polymer might form mixed micelles and crosslinks with other polymer chains, which resulted in a viscosity increase. As all the hydrophobic groups became covered, further surfactant addition resulted in the rupture of the crosslinked systems. Zhang et al.^{43,44} have further investigated interactions between polyacrylamide and surfactants with different headgroup charges. As using polyethoxylated nonionic surfactant (of the type Triton TX-100) with the polymer, they proposed the headgroups were located in the vicinity of the polymer hydrophilic groups (COOH, CONH₂) and were possibly forming hydrogen bonds between the surfactant headgroup and the polymer hydrophilic groups. Furthermore, Cole et al.,⁴⁵ when studying interactions between block copolymeric surfactant and poly-(acrylic acid), reported that this complex involved both hydrophobic interactions between the aliphatic side chains of the polymer and the propoxy-group and hydrogen bonding. From these considerations, it was thought that the polymer-solution viscosity illustrated in Figure 7 might result from such interactions; to verify this hypothesis, a simple polymer-surfactant solution was studied in order to observe such interactions. The polymer previously precipitated into acetone was weighed such that it corresponded to the amount present in the polymer

emulsion and various concentrations of EB were added such that it reproduced the true diluted polymer solution. The results of this experiment are shown in Figure 8.

Contrary to our expectations, there was no evidence of polymer-surfactant interactions. Furthermore, no difference was observed between Atpol 1-731 and NP-6, over the range tested. On the one hand, the concentration range as represented is very low, such that the effects might not be observable. On the other hand, it must be pointed out that the polymer-surfactant model used was an oversimplification of reality, since it did not include the presence of the oil phase or the oil-soluble surfactants used to stabilize the polymer emulsion. The abovementioned diluted polymer solution is a complex organization of three coexisting phases, the polymer is among them and there might be some interactions that were not evidenced as yet.

Polymer-surfactant interactions: effect of the critical micelle concentration

The starkest differences between the diluted polymer solution after inversion and the mixed polymer-surfactant solutions are the complex coexistence of three phases (oil and water phase and surfactants), a mixture of low and high HLB surfactants, and a polymer whose major application is flocculation. Therefore, to

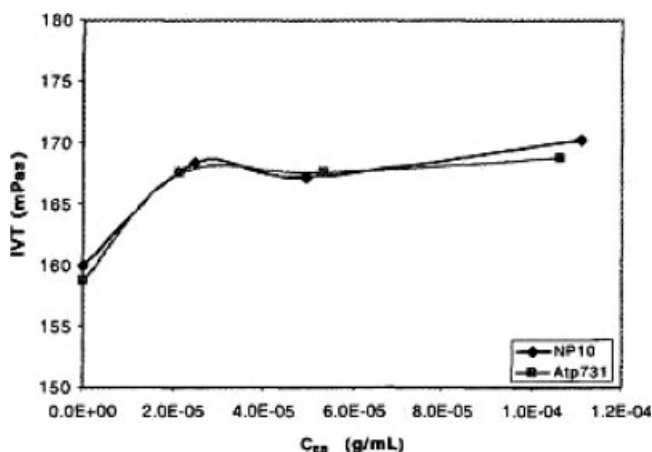


Figure 8 Polymer solution viscosity (IVT) as a function of the EB concentration expressed as g/mL of total aqueous phase.

account for the surfactant influence in the diluted polymer solution its viscosity was plotted as a function of EB concentration in units of the total water phase (the total amount of water contained in the system after inversion). This was necessary in order to emphasize the role played by the inverting surfactant as the critical micellar concentration of pure inverting surfactant was reached. As is reported in Figure 9, the CMC of the nonylphenol-type of inverting was measured at 5×10^{-5} g/mL and coincided with the optimum concentration, while the corresponding CMC for alcohol ethoxylates was 10^{-5} g/mL. Returning to the concept of cooperative and noncooperative association^{41,46} briefly described in the previous section, one might assume that both surfactants used

involved distinct mechanisms of association. In the case of the nonylphenol surfactants, the viscosity increase was observed to start well below the CMC, which might correspond to a cooperative association [Fig. 9(a)]. However, noncooperative associations are also attributed as viscosity increases which occur beyond the CMC, as seen with alcohol ethoxylate type of surfactants [Fig. 9(b)].

Effect of partition coefficient and interfacial activity on inversion

The partition coefficient K_p , defined as the equilibrium ratio of the surfactant concentration in the water phase to the surfactant concentration in the oil phase, was evaluated and compared with the HLB and the inversion efficiency. It has to be mentioned that the data and our discussion cover only nonylphenol polyethoxylated surfactants. The results showed that K_p increased with increasing degree of ethoxylation of the inverting-agent (increasing HLB), as depicted in Table I. Indeed, as HLB increases, the inverting surfactant contains an enhanced percentage of hydrophilic tail whose partitioning promotes its presence into water phase (surfactant-water interactions increase as the amount of ethoxylated group is increased). Furthermore, a comparison of the data from Table I with Figure 9 indicates that partitioning is an important factor in the inversion process. One should note that the best performance was realized by nonylphenol (10)-polyethoxylated (NP-10), which is highly water soluble ($K_p = 3.9$), and that nonylphenol with six ethoxylate units (NP-6), which nearly equipartitions between the

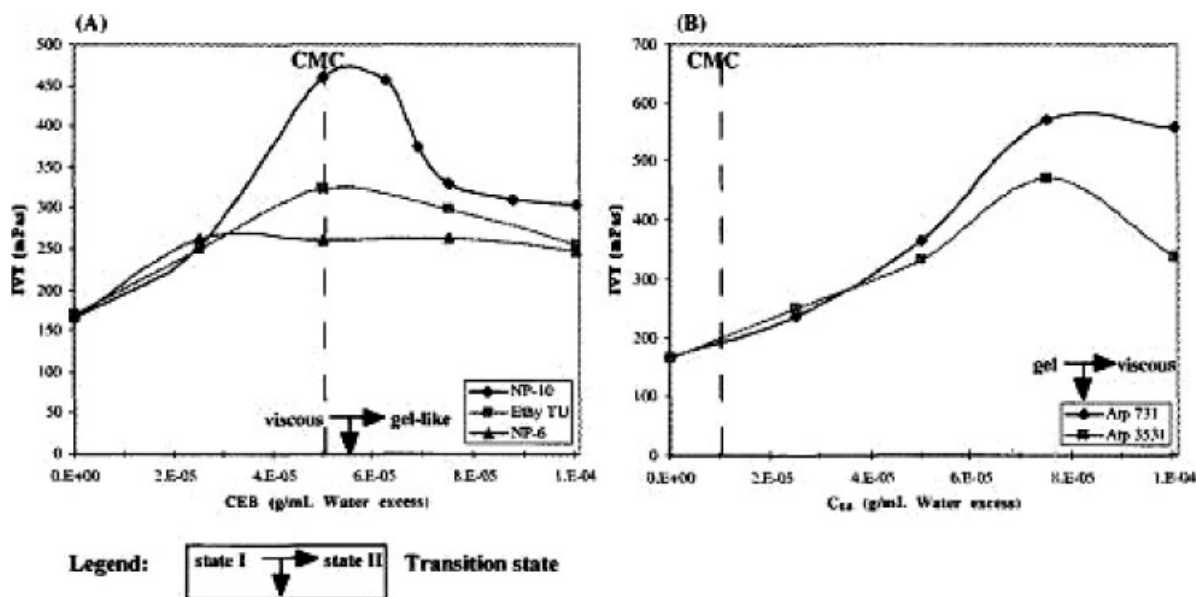


Figure 9 Polymer solution viscosity (IVT) as a function of the EB concentration expressed as g/mL of total aqueous phase (dashed line represents the CMC of the pure surfactant in water).

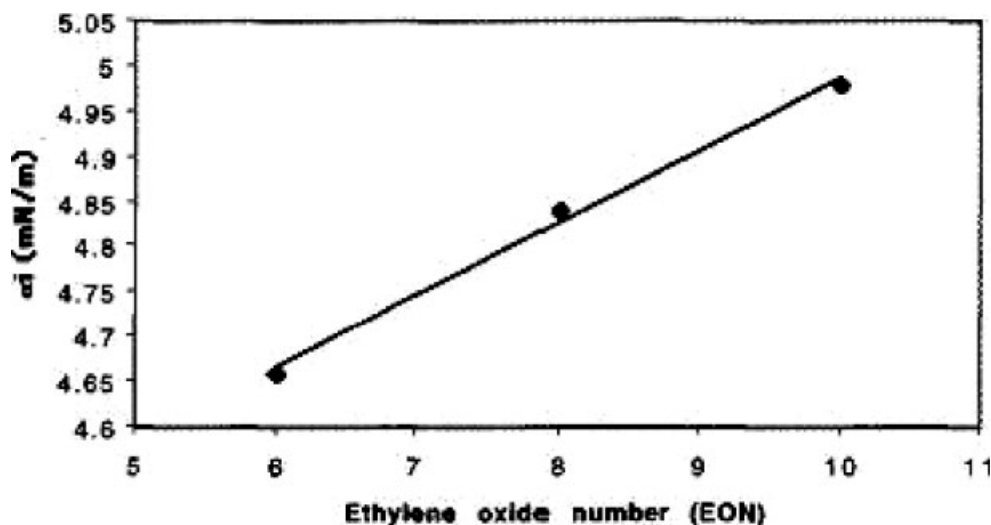


Figure 10 Interfacial activity of polyethoxylated nonionic surfactant as a function of the ethylene oxide number. Data relate only to the NP type of inverting surfactant.

water and oil ($K_p = 1.2$), recorded the worst performance. Such results are contradictory to the optimum value approaching unity, as generally encountered in demulsification.²³ However, it should be pointed out that demulsification and inversion of emulsion are rather two different processes with different applications. In the first case (i.e., demulsification), the process is dealing with a rapid destabilization of the interface such that coalescence is promoted and, as a result, a complete phase separation is obtained.⁴⁷ The necessity to disrupt the W/O interface is of crucial importance and was observed to be most effective with equi-partitioned surfactants (K_p approaching unity), since they may act both from the interior and the exterior of the droplet. This, in turn, drastically reduces the Marangoni–Gibbs effect and, therefore, phase separation.⁴⁸ In the second situation, phase inversion involves a morphology change from W/O to O/W emulsion, which in turn may be achieved by a change of the physicochemical formulation (modifying a variable able to change the affinity of the surfactant for either oil or the water phase) or by a change in the water-to-oil ratio.⁴ Furthermore, Bancroft's rule states that the phase in which the surfactant is most soluble constitutes the continuous phase.⁴⁰ Applying these considerations to phase inversion of polymer emulsions containing EB, it is evident that the surfactant with enhanced hydrophilicity tends to promote the dispersion of oil droplets into water. Therefore, the higher the partition coefficient, the better the inversion, which may justify the necessity for the EB partition coefficient to be higher than unity ($K_p = 1$). These results point to the importance of thermodynamics in phase inversion, as the partition coefficient influences the SAD.

As was presented by Kim et al.,²³ the partition coefficient by itself may not be a definitive parameter to account for demulsification efficiency, since a destabi-

lizing agent is also required to be interfacially active. It is believed that inverting surfactants applied to inversion require similar characteristics, since inversion describes a transition from W/O to O/W (or inversely), and thus the nature of the interfacial phenomena is thought to further influence invertability.

The interfacial activity α_i , determined from the shape of interfacial tension isotherm, is defined as the negative of the derivative of the interfacial tension with respect to the natural logarithm of the concentration and was measured at a water–oil interface for the different inverting surfactants. For simplicity, the model interface did not include the stabilizing surfactants (contrary to the case with polymer emulsions) so as to avoid any undesired interactions with other compounds, such that the interfacial activity was determined by the surfactant. The data are presented in Figure 10. It can be seen that the static interfacial activity correlates with EB performance, independently of the chemistry of the EB employed, with increasing interfacial activity leading to enhanced inversion efficiency. Moreover, considering nonylphenol polyethoxylated surfactants only, interfacial activity showed a linear dependence on the number of ethoxylated groups over the range tested. The way an inverting surfactant acts on the interface in order to ensure inversion upon contact with excess water is not yet understood. Indeed, at the moment there is still no evidence about the location of the water-soluble EB as it is added to the polymer emulsion, although it is thought that it should reach the vicinity of the interface, or transfer within the polymer droplets in the best situation. However, it may be accepted that any interfacially active species may disturb the Marangoni–Gibbs effect, which is responsible for the very slow film drainage and thus enhances the kinetic stability against coalescence.⁴⁹ This happens generally with

demulsification.⁴⁸ The suppression of the Marangoni-Gibbs effect, referred to as interfacial tension gradient, results in an enhanced drainage of the continuous film which flows between the droplets and, as a result, coalescence is facilitated.⁵⁰ One may expect that the inverting surfactants used for the specific purpose of emulsion inversion tends to act in similar way, justifying the need of a highly active agent at the W/O interface such that inversion is promoted.

CONCLUSIONS

For an emulsion breaker dissolved in the continuous organic phase to provide satisfactory inversion, it should be essentially water-soluble with a partition coefficient well exceeding unity and an HLB above 12. A one-to-one correlation exists between the performance of an inverting surfactant and the degree to which it partitions between the aqueous and organic phases. This physical chemical characteristic was more important than the EB chemistry, with nonylphenols providing inversion at a lower concentration compared to alcohol ethoxylates (2 versus 3 wt %). On the other hand, the alcohol ethoxylates provide a higher viscosity following inversion. Above this optimum concentration, lateral interactions may be enhanced which, in turn, promote interfacial film rigidity and reduce the inversion efficiency. In all cases, rheograms of viscosity as a function of the EB concentration revealed a shear thinning region between 0.01 and 100 s⁻¹ followed by an infinite shear-viscosity plateau, as is normal for emulsions.

As phase inversion is dynamic, the initial rate of inversion will influence not only the initial rate of change of viscosity, but also the saturation viscosity plateau (i.e., the ultimate extent of inversion). This depends on the EB chemistry and concentration, and can be represented on the formulation-composition map. Indeed, the map provides a good means of qualitatively describing the catastrophic mechanism of inversion occurring when a polymer emulsion, containing an inverting surfactant, contacts an excess of water.

APPENDIX: THEORETICAL CONCEPTS

From a physicochemical viewpoint, the affinity of the surfactant towards the aqueous phase exactly equals its affinity towards the organic phase for the case of an optimum formulation. The difference between the chemical potential of the surfactant in the oil and water phase is also referred to as the surfactant-affinity difference (SAD), which may be written as:

$$SAD = \mu_w - \mu_o = \Delta G_{o/w} = -RT \ln K_p \quad (A1)$$

where μ is the partition coefficient of the surfactant between water and oil at the corresponding tempera-

ture T , μ is the chemical potential, and ΔG is the difference in the free energy between the oil o and water w phases. Analogously to the experimental correlations for the determination of an optimum formulation,¹⁶ the numerical expression for SAD, as a function of the formulation variables, may be written as a linear combination of independent terms, all of them being measurable and manipulable variables. Therefore, Eq. (A1) can be written as follows:

$$SAD/RT = \alpha' - EON + bS - k ACN - \phi(A) + c_T \Delta T \quad (A2)$$

In this relationship, S is the salinity (wt % NaCl in aqueous solution), ACN denotes the alkane carbon number (a characteristic parameter of the oil phase), $\phi(A)$ is the alcohol concentration, α' is a characteristic parameter of the surfactant structure, and EON is the average number of ethylene oxide groups per molecule of nonionic surfactant. ΔT is the temperature deviation from the reference temperature with b , k , and C_T representing empirical constants dependent on the nature of the system.¹⁶ Each term may be viewed as an energetic contribution to the overall interaction balance. The mathematical formula is expressed as an algebraic sum, which is more convenient than Winsor's ratio R . The sign of SAD indicates the dominant affinity of the surfactant towards oil or water, while its value characterizes the deviation from the optimum formulation. At $SAD = 0$, the surfactant affinity for oil equals exactly that for water, and the optimum formulation is reached. This corresponds to a Winsor R value of 1. With SAD below zero ($R < 1$), the surfactant is predominantly soluble in water. Conversely, with SAD above zero ($R > 1$), the surfactant is predominantly oil soluble.

Additional contributions to eq. (A2) have been reported,^{5,16} however, it is not our purpose to include these here and they will not be discussed further. The present approach points out that, in the vicinity of the optimum formulation, the effect of formulation differences may be described by a unique metric — the surfactant-affinity difference. It will be used as such during this discussion to examine the efficacy of the chemistry of inversion.

Formulation-composition map

The inversion behavior may be described by a formulation-composition map, as shown in Figure A1. The map is divided into six regions, symbolized by a letter and a sign (A^+ , A^- , B^+ , B^- , C^+ , and C^-), which is a characterization largely adopted by other investigators.^{6,17-19} The standard inversion line is represented by a stair-shape and separates the two emulsion morphologies: water-in-oil (W/O) or oil-in-water (O/W) emulsions. A Region A corresponds to midrange values of

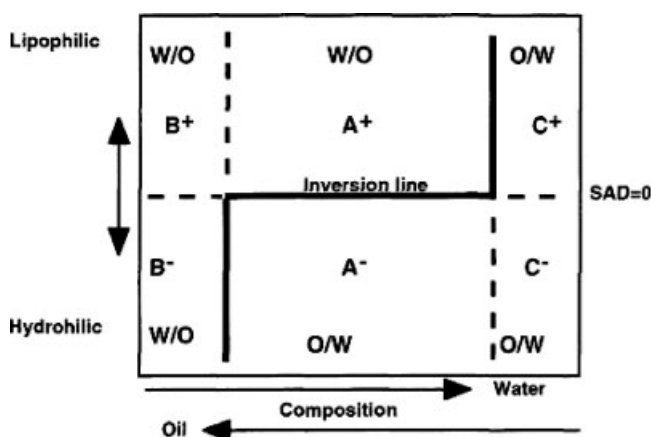


Figure A.1 Formulation–composition map presenting a schematic diagram for phase behavior and emulsion morphology (adapted from François et al.²)

water-to-oil, while regions B and C are associated with low and high water contents, respectively. The boundaries are typically 30% and 70% water for emulsions containing low-viscosity fluids, although they can be quite different in other cases. The formulation effect is depicted by the SAD value sign. A positive value describes the preference of surfactant to oil (lipophilic), while a negative value implies a more hydrophilic surfactant affinity. A^+B^+ and A^-C^- are referred to as “normal” W/O and O/W regions, respectively, because the emulsion type matches the interfacial curvature expected from the wedge theory and similar rules of thumb.⁵ On the other hand, C^+ and B^- describe “abnormal” multiple emulsions of the w/O/W and o/W/O types, respectively. Therefore, the vertical branches (A^+C^+) of the inversion line separate a normal emulsion from an abnormal one.

The surfactant-affinity difference reduces the formulation to a single, thermodynamic, variable. There remain, however, additional degrees of freedom in the formulation that may be considered. These variables capable of affecting the system are the surfactant concentration, the individual phase viscosities, as well as all variables that account for emulsification, such as agitation conditions.⁵ None of these variables significantly influenced the position of the horizontal branch of the formulation–composition map (Fig. A.1), provided that it was located at $SAD = 0$. In contrast, the vertical branch of the inversion line was observed to be affected in such a way that the location may shift and even turn from a vertical to a slanted line. When the vertical portion of the formulation–composition map becomes slanted, this indicates the influence of composition on inversion rather than formulation, which normally dominates. The disposition of the standard inversion line on the bidimensional formulation–composition map that corresponds to the imposed conditions is of crucial importance for the emulsion

maker, since it indicates in a straightforward way where to achieve specific properties, as is explained elsewhere.¹⁶ When examining the wetting behavior of various inverting surfactants as a function of their chemistry, the formulation–composition map will be critical in the interpretation of tendencies.

Dynamic inversion

When an emulsion is subjected to a change in composition (typically expressed either as the water-to-oil ratio) or formulation (a variable able to change the affinity of the surfactant for either oil or water phase), under constant agitation, its representative point is displaced on the formulation–composition map according to a continuous or discrete motion, and leads to different situations:

- If the displacement does not cross the standard inversion line, no morphological change is observed; although other properties of the emulsion are likely to change, depending on the specific characteristics of the regions visited. Such an emulsion shift is applied to adjust the mean value of the emulsion drop size, as well as the emulsion viscosity or stability.⁵
- When the path of the emulsion representative point crosses the standard inversion line and stays on the other side, a dynamic inversion is likely to occur.¹⁷

Investigators have observed⁴ that when a formulation is changed (including temperature) and the horizontal branch separating the normal region A of the map is crossed, then a dynamic inversion occurs precisely at the point of transition across the standard inversion line, which is at the optimum formulation. Such a change takes place independently of the position and direction of the change. This behavior is in accordance with the extremely low interfacial tension and low emulsion stability exhibited in this region.²⁰ Indeed, it may be thought that any emulsion formed, in this region, breaks up very quickly, followed by a rapid reformation because of the prevailing low interfacial tension. Furthermore, Fillous et al.²¹ have demonstrated that mass transfer was very fast at this location of the formulation–composition map, such that any surfactant shift from one phase to the other is likely to occur quickly. At this stage, these rapid changes are equivalent to instantly equilibrated phenomena in which case the physicochemical conditions prevail over the kinetic or time-dependent effects.^{3,4}

When crossing the vertical branch, phase inversion is achieved by a change in water-to-oil ratio. This is the type of behavior observed when inverting an inverse-emulsion, in the presence of an inverting surfactant, in an excess of water. Experimental evidence

indicated that a change in the water-to-oil ratio (WOR) produced by addition, under constant agitation, of a certain amount of one of either phase (water or oil) to the preexisting emulsion showed quite different characteristics. Emulsion inversion does not take place immediately nor at the same water-to-oil ratio.²² Furthermore, the emulsion inversion line depends on whether WOR is increasing or decreasing. If the change is an increase in the internal phase fraction from a "normal" to an "abnormal" emulsion, that is, from zone A^+ to zone C^+ at $SAD > 0$ and from A^- to B^- at $SAD < 0$, the dynamic inversion delay characteristic tends to increase the width of region A. Conversely, any change from an abnormal emulsion to a normal one (from C^+ to A^+ at $SAD > 0$ and from B^- to A^- at $SAD < 0$) results in a reduction of region A. Moreover, phase inversion depends on the formulation: the farther from $SAD = 0$, the larger the compositional change the emulsion can take before inversion happens (Fig. A.2). The inversion process, based on the addition of nonylphenols to polyacrylamide-based inverse emulsions, is shown to follow the behavior noted in Figure A.2. Given this, formulations which are close to the optimum SAD of zero will provide the most effective inversion. Though laborious to understand, the formulation-composition maps permit us to comprehend the

reasons for the inversion optimums which will be observed for the specific system under investigation in this publication. They also permit us to explain the type of inversion (i.e., if catastrophic) as well as the influence, if any, of the kinetics of inversion mediated by, for example, the rapid increase in viscosity.

The existence of a displacement in both directions of crossing implies that the standard inversion line lies between the dynamic inversion line for the two compositions sweeps, that is, at an intermediate position within the triangular zones (Fig. A2) resulting from the superposition of the dynamic inversion boundaries.¹⁹ These wedge-shaped zones indicate a hysteresis, since any of the two emulsion morphologies may coexist within it.²² Hysteresis is linked with irreversible instability phenomena and is sometimes referred to as catastrophic, since there is a sudden change in the behavior of the system as a result of gradually changing conditions. It is thus convenient to denote it as catastrophic inversion.⁹ (Phase inversion induced by changing the phase-volume fraction shows all the characteristics of a so-called cusp-catastrophe: bimodality, inaccessible behavior, sudden jumps, hysteresis, and divergence.¹⁵) The resulting type of emulsion in the hysteresis region is thus dependent on the previous history of the system, i.e., the change in water-to-oil ratio. Such a

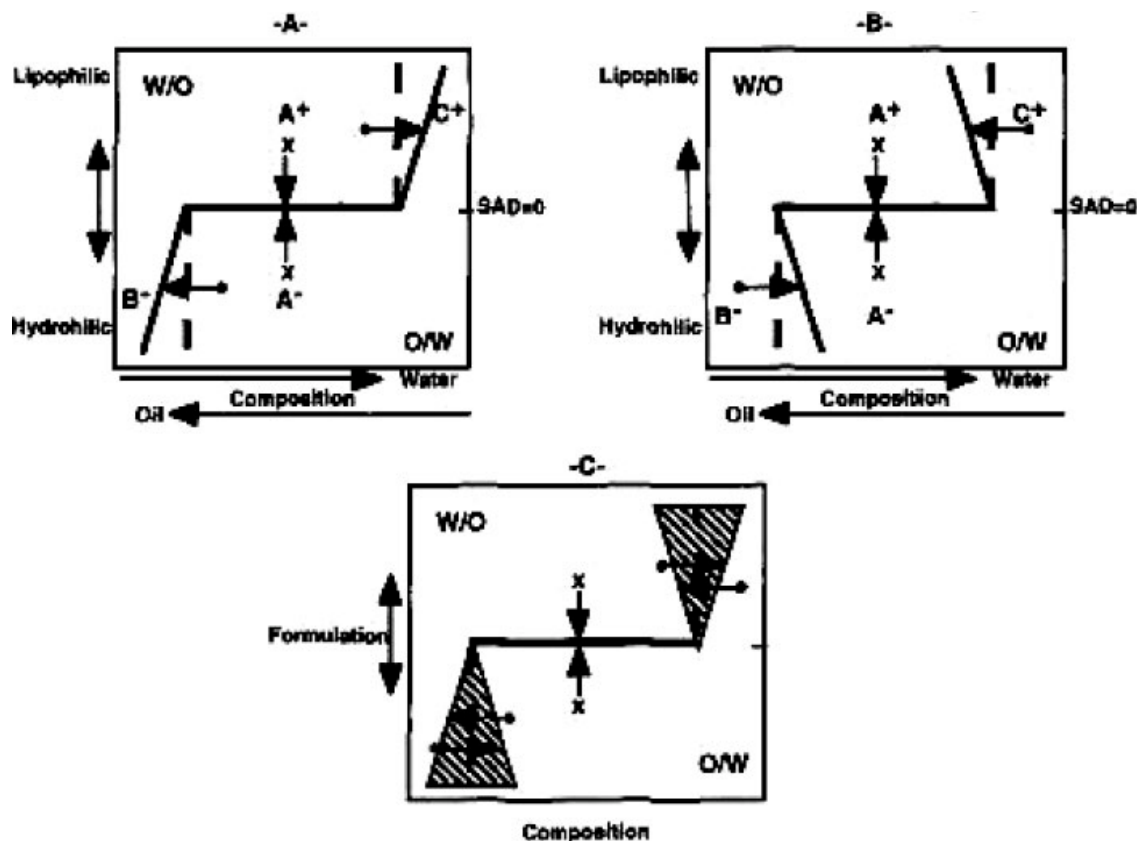


Figure A.2 Dynamic inversion pattern (adapted from Salager¹⁷). Presentations (A) and (B) illustrate dynamic inversion boundaries. The shaded area in (C) shows this hysteresis and indicates a zone of zone of coexisting morphologies.

hysteresis is key in the interpretation of the role of wetting-agent chemistry in the inversion of polymeric inverse-emulsions.

References

- Bourdillon, L.; Hunkeler, D.; Wandrey, C. *Progr Colloid Polym Sci Analyst Ultracentrifugation* 2006, VIII, 131.
- François, G.; Srinivisan, B.; Bonvin, D.; Hernandez Barajas, J.; Hunkeler, D. *Ind Eng Chem Res* 2004, 43, 7238.
- Salager, J.-L., Anton, R. E. *J Dips Sci Tech* 1983, 4, 313.
- Salager, J.-L. In *Encyclopedia of Emulsion Technology*; Becher, P., Ed.; M. Dekker: New York, 1980, pp 80–129.
- Salager, J.-L. *Ind. Eng Chem Res* 2000, 39, 2665–2676.
- Brooks, B. W.; Pelton, R. H. *Colloids and Surfaces*, 1991, 58, 13.1–148.
- Brooks, B. W.; Richmond, H. N. *Chem Eng Sci* 1994, 49, 1065.
- Brooks, B. W.; Richmond, H. N. *Chem Eng Sci* 1994, 49, 1843.
- Dickinson, E. *Colloid and Interface Sci* 1981, 84, 284.
- Dickinson, E. *Colloid and Interface Sci* 1982, 87, 416.
- Vaessen, G. E. J.; Vissches, M.; Stein, H. N. *Langmuir* 1996, 12, 875.
- Lirn, S. K.; Bloomquist, A.; Schaper, R. U.S. Pat. 4,147,681.
- Ellwanger, R. E. U.S. Pat. 4,115,340.
- Venema, G. U.S. Pat. 3,852,234.
- Vaessen, G. B. J.; Stein, H. N. *Colloid and Interface Sci* 1995, 176, 378.
- Salager, J.-L. In *Pharmaceutical Emulsions and Suspensions*; Marti-Mestres, F. N., Ed.; Marcel Dekker: New York, 2000; pp 20–72.
- Salager, J.-L. In *Pharmaceutical Emulsions and Suspensions*; Marti-Mestres, F.N., Ed.; Marcel Dekker: New York, 2000; pp 73–121.
- Binks, B. P.; Lumsdon, S. O. *Langmuir* 2000, 16, 2539.
- Silva, F.; Pena, A.; Minona-Perez, M.; Salager, J. L. *Dynamic Colloids and Surfaces A* 1998, 132, 221.
- Salager, J.-L.; Grosso, J. L.; Eslava, M. A. *Rev Tecn INTEVEP* 1982, 2, 149.
- Cardenas, A.; Rouvior, J.; Salager, J. L. Fillous, L. *Surfactants Deterg* 1999, 3, 303.
- Becher, P. *Soc. Cosmo Chem* 1959, 141.
- Kim, Y. H.; Wasan, D. T. *Ind. Eng Chem Res* 1996, 35, 1141.
- Nornmensen, P. A. *Physical Rev E* 1999, 59, 3147.
- Papir, Y.; Krieger, I. *Colloid and Interface Sci* 1970, 34, 126.
- Otsubo, Y.; Prud'homme, R. K. *Rheologica Acta* 1994, 33, 29.
- Windhab, E. 1st Int Symp Food Rheology and Structure, Zurich, 1997.
- Woods, M. E.; Krieger, I. *J Colloid Inter Sci* 1970, 34, 91.
- Evans, D. F.; Wennerstrom, H. In *Colloidal Domain Where Physics, Chemistry, Biology, and Technology Meet*; Wennerstrom, E. A., Ed.; Wiley VCR: New York, 1999; p 539–599.
- Salager, J.-L., Márquez, M.; Graeraa, A.; Lachasse, J. *Langmuir* 2000, 16, 5534.
- Zaki, N. N.; Abdel-Raouf, M. E.; Abdel-Azim, A.-A. A. *Monatshette für Chemie*, 1996, 127, 621.
- Goldszal, A.; Bourrel, M. *Ind Eng Chem Res* 2000, 39, 2746.
- Kim, Y. H. *J Disp. Sci Tech* 1996, 17, 33.
- Griffin, W. C. *J Soc Cosmet Chem* 1949, 1, 311.
- Shetty, C. S.; Nikolov, A. D.; Wasan, D. T. *J Disp Sci Tech* 1992, 13, 121.
- Cooper, D. G. *Canadian J Chem Eng* 1980, 58, 576.
- Binks, B. P.; Fletcher, P. D. I.; Ye, X.; Lu, J. R. Averyard, R. In *A Fundamental and Practical Approach*; Sjoblom, J., Ed.; Kluwer Academic: Amsterdam, 1992; p 97–110.
- Abdel-Azim, A.-A. A.; Zaki, N. N.; Maysour, N. E.-S. *Polym Adv Technol* 1998, 9, 159.
- Laurence, A. S. C.; Killner, K. W. *J Inst Petrol* 1948, 34, 28.
- Bancroft, W. D. *J Phys Chem* 1913, 17, 501.
- Panmai, S.; Prud'homme, R. K.; Peiffer, D. G. *Colloids and Surfaces A*, 1999, 147, 3.
- Hulden, M. *Colloids and Surfaces A*, 1994, 82, 263.
- Zhang, J. Y. *Colloids and Surfaces A* 1994, 88, 33.
- Zhang, J. Y. *Colloids and Surfaces A* 1998, 132, 9.
- Cole, M. L.; Whateley, T. L.; *J Colloid and Interface Sci* 1996, 180, 421.
- Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D.; Ananthapadmanabhan, K. P.; Ubson, D. J.; Kim, Y. H.; Niklov, A. D.; Shetty, C. S.; Eds.; CRC Press: Boca Raton, FL, 1993; pp 203–273.
- Bhardwaj, A.; Hartland, S. *J Disp Sci Tech* 1993, 14, 541.
- Krawczyk, M. A.; Wasan, C. S.; Shetty, D. T. *Ind Eng Chem Res* 1991, 30, 367.
- Hartland, S.; Jeelani, S. A. K. *Colloids and Surfaces A*, 1994, 88, 289.
- Breen, P. J. In *Emulsions and Emulsion Stability*; Sjoblom, J., Ed.; Marcel Dekker: New York, 1996.