
5 Phase Inversion Studies as a Tool for Optimization and Characterization of Surfactant Mixtures in Specific Oil/Water Systems

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5.1 INTRODUCTION

In the development work of new emulsifiers or new mixtures of emulsifiers the need for versatile characterization tools is urgent. In line with this many high throughput techniques are introduced especially within the industries. The tool described in this chapter quickly provides information and understanding of the nature of the investigated surface activity of mixtures of emulsifiers from

the industrial world. Another advantage is the direct information obtained about the behavior of the system when the hydrophilic/lipophilic balance is changed.

In many applications the simultaneous presence of a polar and a nonpolar solvent is desirable. When oil and water are mixed under stirring, an emulsion is formed. The resulting emulsion often needs to be stable. This stability is achieved by the addition of one or several emulsifiers. The problem of selecting the best system for this purpose is ubiquitous. Solutions have been sought in describing the structure of the emulsifier in terms of hydrophilic–lipophilic balance (HLB) (1), or critical packing parameter (CPP) (2). These attempts have not included the influence of other parameters, such as oil, temperature, and salt, which play important roles for emulsion stability. Shinoda (3) works with temperature effects and uses phase inversion temperature (PIT) to describe the function of emulsifiers, mainly of ethoxylated nonionic surfactants. Lately, a systematic approach to use the PIT has been described (4) under the abbreviation CAPICO (calculation of phase inversion in concentrated emulsions).

Typical for an emulsion, stabilized by nonionic emulsifiers, which is heated or cooled beyond the phase inversion temperature, is its change in morphology: the emulsion inverts by going from an oil-in-water (O/W) to a water-in-oil (W/O) emulsion or vice versa. This means that the spontaneous curvature, H_o , of the interfacial film changes sign and passes a flat form where $H_o = 0$. This point is the balanced point or optimal point where, at thermodynamic equilibrium, a bicontinuous microemulsion is formed and the interfacial tension is at its minimum.

Davies writes: “The spontaneous mean curvature, H_o , determines whether the interfacial film wants to curve onto its oil or its water side or prefers to be flat” (1). That this tendency plays an important role in deciding if an O/W or a W/O emulsion will be formed, even though the curvature of an emulsion droplet is much less than that of a micelle, has been re-emphasized by Kabalnov and Wennerström (5) in the late 1990s.

It has also been shown by Pérez et al. (6) that the most stable emulsions are to be found at a specific distance from the balanced situation where $H_o = 0$ or, in his terminology, $SAD = 0$ (surfactant affinity difference). Thus it is important to find the balanced point of the actual emulsion or formulation that is being optimized.

The aim of the work reported here is to find a practical method to determine the balanced or optimal point of a system which can be employed with all types of emulsifiers, including those that are not temperature or salt sensitive. An automatic titration procedure is used by which a co-surfactant is added to a surfactant–oil–water (SOW) blend under stirring at constant temperature (see Figure 5.1). The morphology changes of the emulsion are monitored by means of conductivity. A steep conductivity decrease is observed when the emulsion inverts from O/W to W/O and vice versa when the morphology changes from W/O to O/W. Three important aspects are:

1. By using reference compounds like isomerically pure ethoxylates and the same co-surfactant and oil, the behavior of any other surfactants can be compared to systems with known HLBs or whatever traditional description concepts that are familiar to the user.
2. If instead the oil phase is changed and the same surfactant pair is used, the titration will provide information about the character of the oil, whether its behavior is more hydrophilic or more hydrophobic than the reference oil.
3. In many applications the surfactant blend resulting in the lowest interfacial tension is the most efficient. Since the inversion point is the point of minimum interfacial tension, the titration method is also a means of optimizing formulations in specific areas like cleaning or soil remediation.

Three practical examples will be given to illustrate the three aspects mentioned above.

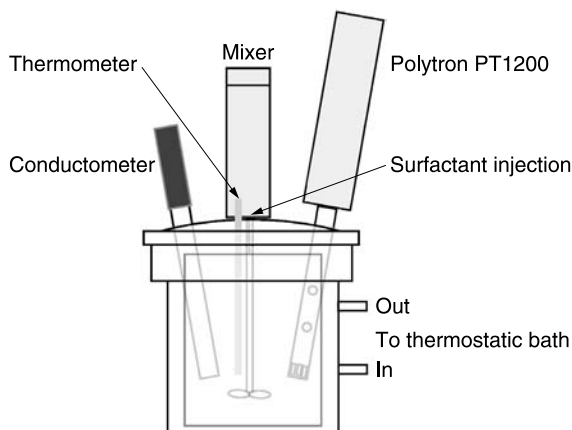


FIGURE 5.1 Experimental set-up for the co-surfactant titration followed with conductometry. Commercially available as the Multi Parameter Scanning (MPS) instrument from Scanalys (www.scanalys.com), with possibilities to measure turbidity, pH, conductometry, and viscosity simultaneously.

5.2 EXPERIMENTAL

Laboratory products from Akzo Nobel Surface Chemistry AB were:

- Branched C10 alcohol of Guerbet type with 3, 5, 8, and 10 ethylene oxide units, both narrow and broad range distribution, referred to as BrC10E(m) narr or broad
- Straight C10 alcohol with 3, 5, 8, and 10 ethylene oxide units, both narrow and broad range distribution, referred to as 1D E(m) narr or broad
- Glucosides of the same two alcohols with an average degree of polymerization of 1.6

Commercial products from Akzo Nobel Surface Chemistry AB were:

- Berol ox 91-6 and 91-8 which are made from C9–11 alcohol with 6 or 8 ethylene oxide units, broad range
- Berol 992, alkoxyated short chain fatty alcohol with cloud point 80 °C in 10% NaCl
- Berol 822, calcium dodecylbenzene sulfonate, 60% in butanol
- AG 6210, a C8/C10 glucoside with an average degree of polymerization of 1.6
- Berol 532, C11 with two ethylene oxide units

Other products were: isomerically pure C10E5, C10E7, and C10E8 (Sigma Aldrich and Fluka), Span[®] 80 and sorbitan monooleate (Fluka), n-decane (>95%) (Merck), Danish winter diesel (Statoil), Solvesso 150D (ExxonMobil), and methyl laurate (Merck). Water was distilled and de-ionized.

To determine the *critical micelle concentration*, surface tension was measured on a KSV unit with a Sigma 70 program using the Du Noüy ring method.

The *contact angle* was measured on Parafilm[®] with a FTÅ200 instrument in a climate controlled room ($T = 21 \pm 1$ °C, $45 \pm 10\%$ rH).

To determine *cloud points*, mixtures of 1.0 wt% surfactant in distilled water, aqueous NaCl (2.0 g/l; 0.034 M), or 11% BDG were prepared. The mixtures that were clear at room temperature were heated in a water bath until the mixture became turbid. The mixtures that were turbid at room

temperature were placed in ice until the mixture became clear (or no difference in appearance could be determined in the 0–100 °C domain). In both cases cloud points were determined upon cooling.

The *foam height* was measured in a winding equipment with fixed measuring cylinders (500 ml) with 200 ml of surfactant solutions in each, which is turned around 40 times during 1 min. The foam height was recorded immediately and after 1 min.

Conductivity measurements were carried out according to a typical example taken from the study of decyl ethoxylates, Span[®] 80, and decane/water, as follows.

n-Decane (24.25 g; 0.15 mole), aqueous NaCl (24.25 g; 2.0 g NaCl/L; 0.034 M), and surfactant (1.50 g) were homogenized in a thermostatted glass vessel. Temperatures at the inversion point were in the region $24.6\text{ °C} \leq T \leq 26.3\text{ °C}$. The apparatus used to homogenize the mixture in the vessel was a stirring device (brand unknown) at maximum stirring speed and an Ultra Turrax (Polytron PT 1200) at a stirring speed >15,000 rpm (level 5). Conductivity was measured with a Pt electrode (Metrohm 712 conductometer) and temperature was measured with a thermometer (Physitemp BAT-10) while a mixture of Span[®] 80/n-decane (8/3 w/w) was titrated in using a dosimat (Metrohm 665) at a dosing rate (dr) of 0.15 ml/min. [Figure 5.1](#) shows the experimental setup of the automatic titration technique.

Some measurements were performed on Scanalys[®] equipment. It is essentially the same experimental setup as above (www.scanalys.com), but one single stirrer was used at 225 or 300 rpm. Sometimes a complementary magnetic stirrer was introduced. The co-surfactant was titrated in with a dosing rate of 4.44 $\mu\text{l/sec}$.

5.3 RESULTS AND DISCUSSION

5.3.1 CHARACTERIZATION OF DECYL ETHOXYLATES AND DECYL GLUCOSIDES

A set of ethoxylates from straight chain and Guerbet branched decanol was made. Different catalysts were used to obtain broad or narrow distribution. Typical distributions are shown in [Figure 5.2](#).

5.3.1.1 Emulsion Inversion

Since the total concentration of surfactant is increased during the titration, the titration path is somewhat diagonal as is shown in [Figure 5.3](#). The inversion will take place when passing over the three phase region in the so-called “Kahlweit fish” (7). Both surfactant concentration and character is varied. The region where three phases, an excess oil phase, a surfactant phase, and an excess water phase, occur often has the form of a fish body. Polydispersity of the surfactant may result in a skewed fish body, for example bent upwards or downwards (8). To successfully apply the technique described here it is practical to know what the relative position in the phase diagram is of the initial composition compared to the fish body. Otherwise there is the risk of missing the inversion point, either starting too far below the required ratio of hydrophobic co-surfactant to total surfactant (α) (= below the fish body) or with too low total surfactant concentration (γ) (= before the fish body) to bring about the inversion.

In principle, the nature of the surfactant(s) can be varied by temperature (nonionics), salt (ionics), or by addition of a co-surfactant (all surfactants). We apply the latter, most universal, technique to invert an emulsion from O/W to W/O (addition of a relatively hydrophobic co-surfactant) or from W/O to O/W (addition of a more hydrophilic co-surfactant).

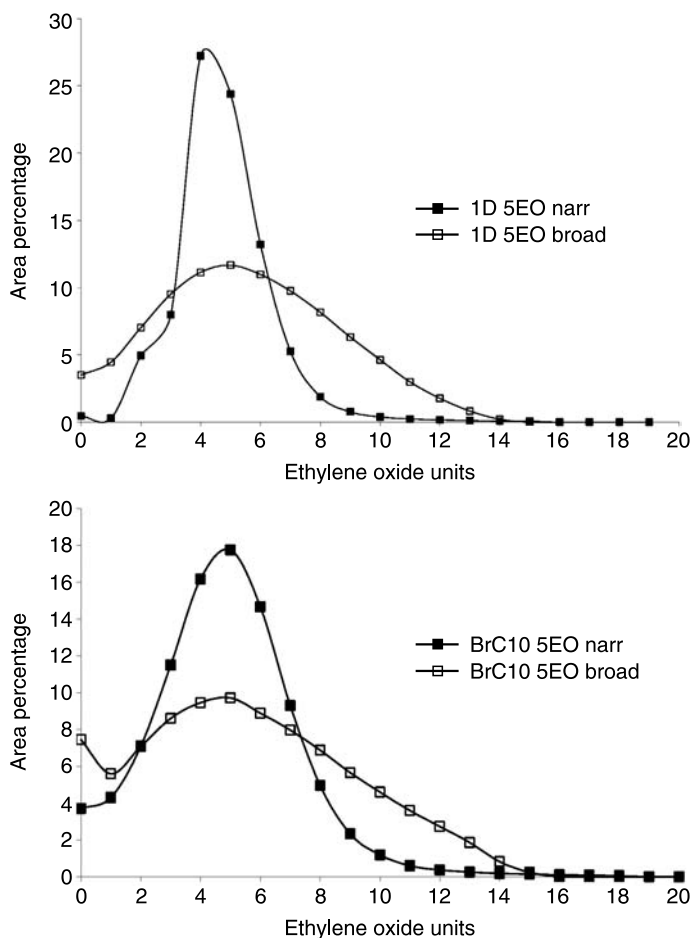


FIGURE 5.2 (a) Ethylene oxide distributions of decyl alcohol ethoxylates, broad and narrow range. (b) Ethylene oxide distributions of branched decyl alcohol ethoxylates, broad and narrow range.

Most of the nonionics studied here are hydrophilic enough to give a water continuous emulsion when stirred. Sorbitan monooleate, Span[®] 80, was chosen as co-surfactant (HLB = 4.3, Ref. 3) and decane as the oil phase. The inversion was followed from water continuous (O/W) to oil continuous (W/O). A typical well-behaved run is shown in Figure 5.4 for a 1D E3 broad range.

Many of the titrations showed fine structure (see Figure 5.5), indicating areas with liquid crystalline phases as one of several phases in the phase diagram. For a detailed understanding equilibrium studies have to be performed. However, as the systems become better known the interpretation of these fine structures become more and more direct.

To be able to work with the results of the titration an evaluation technique was established. An example of this is given in Figure 5.5. Linear fits to the first and last part of the steep conductivity drop in a plot of conductivity as a function of the amount of added co-surfactant are constructed (Figure 5.5). IP_{upper} is determined as the breakpoint of a horizontal line through the maximum in the conductivity curve and a linear fit to the first portion of the steep drop in

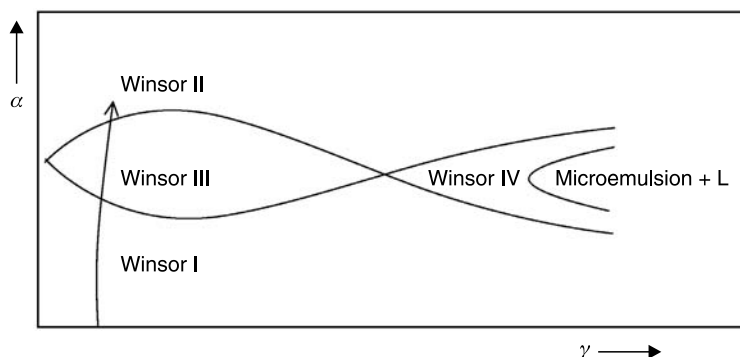


FIGURE 5.3 Schematic representation of a typical titration path (arrow) during the conductivity scan with the automatic titration technique; α = co-surfactant/total surfactant concentration (w/w%), γ = total surfactant concentration (w/w%).

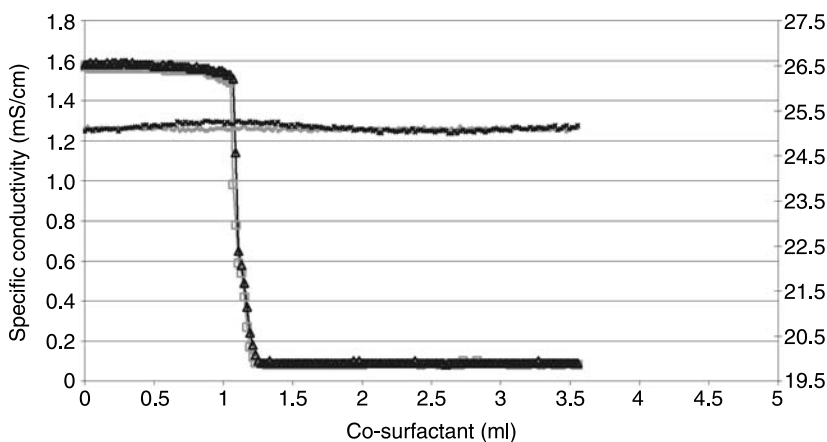


FIGURE 5.4 Conductivity scan for 1D E3 broad range with Span-80/n-decane/NaCl/water ($T = 25.0^\circ\text{C}$, $dr = 4.44 \mu\text{l/s}$, $ss = 300 \text{ rpm}$); temperature is shown on the right axis, (\square) and (\triangle) correspond to two different measurements on the same system.

conductivity. IP_{lower} is the amount of added co-surfactant in milliliters at the breakpoint of a horizontal line through the minimum in conductivity and a linear fit to the last portion of the steep drop in conductivity. The average of these two values can then be used as the “inversion point.”

In [Figure 5.6](#) all the inversion points for the four series of ethoxylated surfactants, the isomerically pure ones and the alkyl glucosides, are gathered in terms of wt% of Span[®] 80 of the total surfactant blend (α) versus the degree of polymerization.

If less co-surfactant is needed to invert the emulsion, the surfactant (mixture) itself may be described as more hydrophobic. In this sense one could say that the surfactants based on a branched hydrophobe in most cases are more hydrophobic; see for instance Br C10 glucoside and Br C10E5 narrow or Br C10E8 narrow as compared to the corresponding straight C10 based ones.

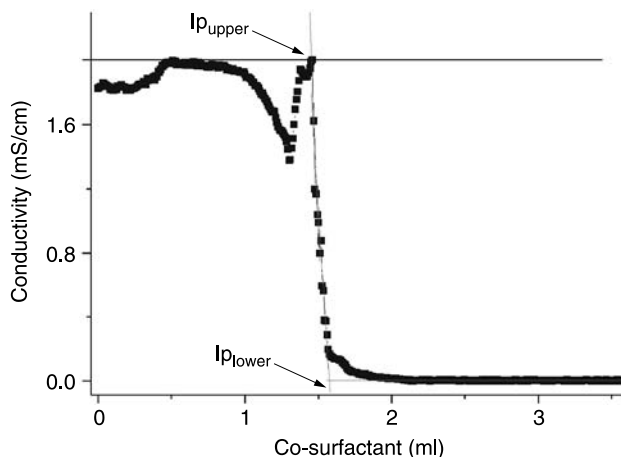


FIGURE 5.5 Linear fits to the first and last part of the steep conductivity drop in a plot of conductivity as a function of the amount of added co-surfactant with 1-decyl glucoside/n-decane/water/NaCl/Span® 80 ($T = 25\text{ }^{\circ}\text{C}$, $dr = 0.15\text{ ml/min}$, $ss > 15,000\text{ rpm}$) to be used for establishing upper and lower inversion points.

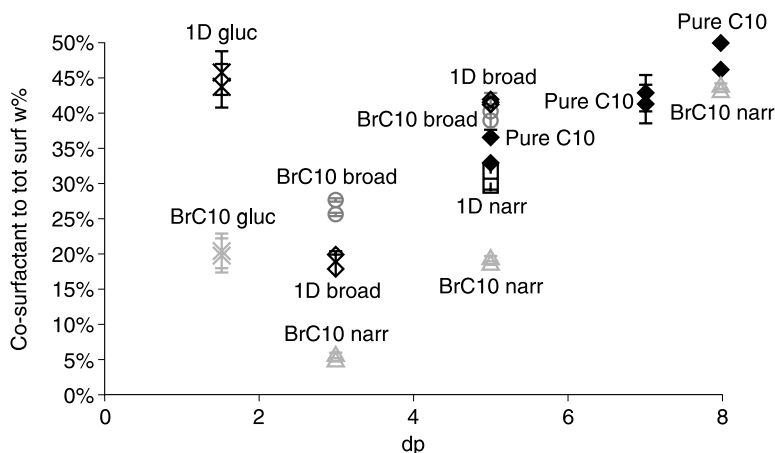


FIGURE 5.6 Inversion points (IP_{upper} and IP_{lower}) as a function of the degree of polymerization of technical grade alcohol ethoxylates, technical grade alkyl glucosides, and isomerically pure alcohol ethoxylates with 5, 7, or 8 EO units. Error bars indicate the deviation of two individual measurements on the system from the average value.

When only 3 moles of ethylene oxide are added the remaining, unreacted, alcohol in the mixture will disturb the overall picture since that alcohol will dissolve in the oil phase and not contribute to the interfacial layer of emulsifiers. Ethoxylation of a branched alcohol yields more unreacted alcohol compared to the reaction with a straight chain one due to steric hindrance. Thus the actual active content of emulsifier will be significantly decreased and the blend will behave in a more hydrophilic manner than is expected from the amount of ethylene oxide added.

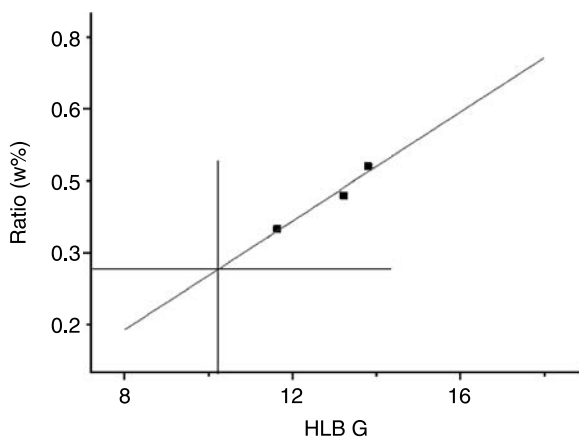


FIGURE 5.7 Extrapolation of a linear fit on the inversion points (average of upper and lower) as a function of the HLB number (Griffin) of pure $C_{10}E_m$ alcohol ethoxylates.

Another general conclusion is that the broad range surfactants seem to be more hydrophilic than the narrow range.

An example of how the characterization via emulsion inversion can be compared to commonly used concepts is given in Figure 5.7. Extrapolation of a linear fit on the inversion points (average of upper and lower) as a function of the HLB number (Griffin) of pure $C_{10}E_m$ alcohol ethoxylates is shown. The equation obtained in this manner provides a way to determine the equivalent HLB number of any (mixture of) surfactant(s) once its inversion point in the same system (i.e., the same temperature, pressure, type of oil) is established.

5.3.1.2 Other Physicochemical Properties

5.3.1.2.1 In Water Solution

5.3.1.2.1.1 Cloud Points

Often the nonionic surfactants are characterized by their cloud points (C.p.), i.e., the temperature at which they have become so hydrophobic that they phase separate from water. These measurements are performed without the presence of a hydrophobic phase wherein a high amount of alcohol may dissolve. The resulting cloud point would thus give a description of the actual hydrophobicity of the technical nonionic surfactant. The cloud points for the set of nonionics studied here is shown in Figure 5.8. The measurement is performed in a mixture of butyl diethylene glycol and water to get a C.p. between 0 and 100 °C for all the products. The general conclusion also here is that the branched hydrophobes give more hydrophobic products than the straight chain ones. Differences between distributions are leveled out in this medium.

The glucosides usually do not show any cloud points except in very special cases and thus can not be characterized in this way. Their solubility increases slightly with temperature.

5.3.1.2.1.2 Critical Micelle Concentration

In Figure 5.9 the dependence of the critical micelle concentrations (CMCs) on the chemical structures is shown. As expected (9), the CMC increases for the same type of surfactant with

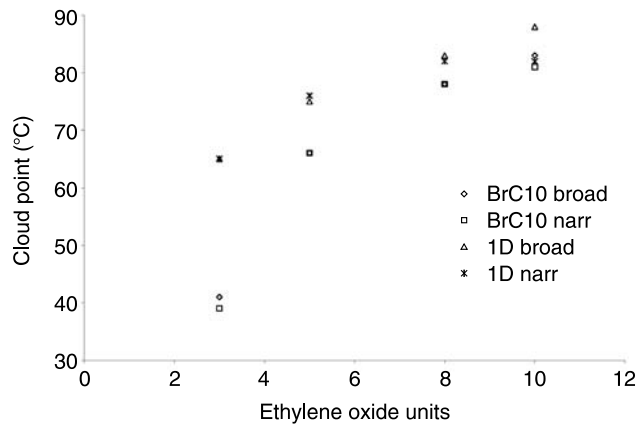


FIGURE 5.8 Cloud point (CP) as a function of the average number of ethylene oxide units $\langle m \rangle$ of 1.0 w% solutions of alcohol ethoxylates with $\langle m \rangle \geq 5$ in 11% butyl diethylene glycol.

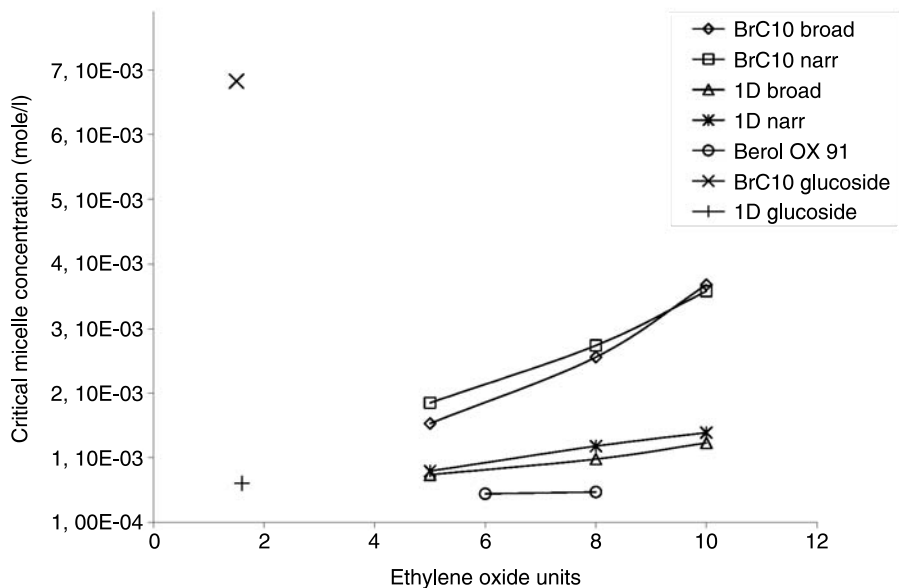


FIGURE 5.9 Critical micelle concentrations of technical grade alcohol ethoxylates and alkyl polyglucosides as a function of degree of polymerization of the head group ($T = 21 \pm 1^\circ\text{C}$).

increasing $\langle m \rangle$ indicative of the increasing hydrophilicity of the surfactant monomer. Moreover, the steric repulsion between the surfactant head groups that form the micelles increases with increasing $\langle m \rangle$ (average length of the EO chain).

Generally the branched products have higher CMCs than the straight chain ones. The first explanation that comes to mind is the packing parameter (CPP). The packing parameter of surfactants with straight chain hydrophobes is more favorable for the formation of (spherical) micelles than is the case for branched hydrophobes.

There is also a small difference between narrow and broad distributions. The broad range surfactants have slightly more freedom in packing the different homologs into the micelles resulting in slightly lower critical micelle concentrations.

For comparison two commercial products based on a C9–11 alcohol blend are shown, which both have lower CMCs than the pure C10 types due to the heterodispersity of the hydrophobe, again giving more freedom in packing the different homologs into the micelles.

5.3.1.2.2 Properties at the Air/Water Interface

5.3.1.2.2.1 Area per Molecule at the Air/Water Interface

By replotting the surface tension versus log concentration data, the area per molecule (a_o) at the air/water interface as a function of $\langle m \rangle$ is obtained (Figure 5.10).

Clearly, a_o increases with increasing length of the EO chain for all types of surfactants except for the broad range Guerbet alcohol compounds. A similar reasoning as for the critical micelle concentration is valid here. Due to the increase in hydration of the head group with increasing length of the EO chain, there is less free energy to be gained upon transfer of the surfactant from the bulk phase to the air–water interface. Moreover, larger head groups simply need more space. Therefore, with increasing $\langle m \rangle$ the equilibrium between surfactants in the bulk and at the interface shifts towards the bulk phase.

Both branching of the hydrophobe and broadening of the EO distribution has an influence on the adsorption:

- Surfactants with the same type of hydrophobe show similar area per molecule at the air/water interface for small head groups. Branched hydrophobes are bulkier and need more space.
- Surfactants with the same type of ethylene oxide distribution show similar a_o values for bigger head groups, that is, the packing of the hydrophilic part at the interface determines the behavior.

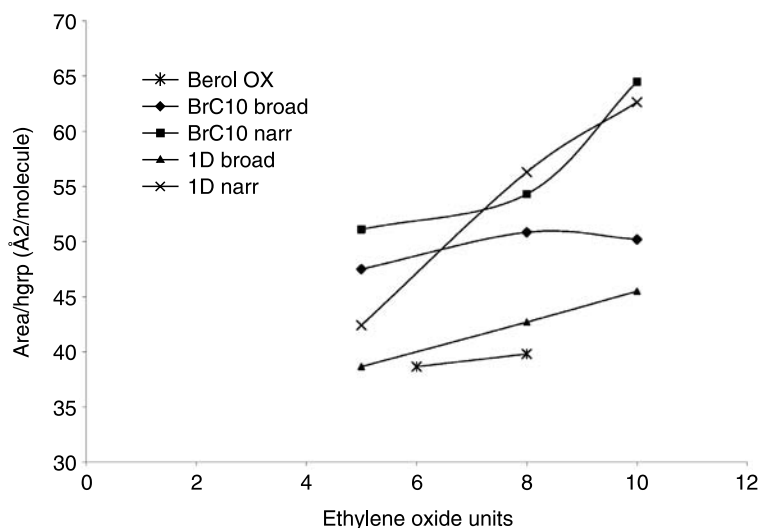


FIGURE 5.10 Area per molecule at the air/water interface as a function of the average number of ethylene oxide units.

Thus the influence of the hydrophobe dominates for smaller head groups and the heterodispersity of the EO chain is the dominant factor for larger head groups. This reflects the increase in the size of the head group relative to the hydrophobe with increasing amounts of EO. It is obvious that broad range surfactants have smaller areas per molecule than narrow range surfactants. Most probably this is a result of the packing advantages of a broader EO distribution.

5.3.1.2.2.2 Surface Tension at the Critical Micelle Concentration

More information to be gained from the CMC curves is the surface tension at or above CMC (see Figure 5.11). Surface tension increases with increasing amounts of EO, except for the broad range Guerbet alcohol based compounds. For the same type of hydrophobe in the surfactant, the smaller the head group, the more surfactant adsorbs at the interface and the lower the surface tension. Note, however, that the special behavior for the branched C10 broad range compounds is also found in the area/molecule graph.

The most striking feature is that the Guerbet alcohol based surfactants show lower surface tension values in spite of the relatively low adsorption when compared to the straight chain surfactants. Apparently, the branched surfactants form a more hydrophobic surfactant layer at the air–water interface.

It can be speculated that the reason for this might be as follows. The branch may be positioned planar to the interface, while the rest of the surfactant tail is positioned lateral to the interface. Therefore, the branch reduces the contact between water and air resulting in lower surface tensions for branched surfactants.

5.3.1.2.2.3 Foam

The foam was measured for the different C10E5s and the corresponding glucosides at 20 and 50 °C (Figure 5.12). The branched alcohol based surfactants all show much less stable foam, probably due to less elasticity of the foam lamella created from the less well packed branched surfactants.

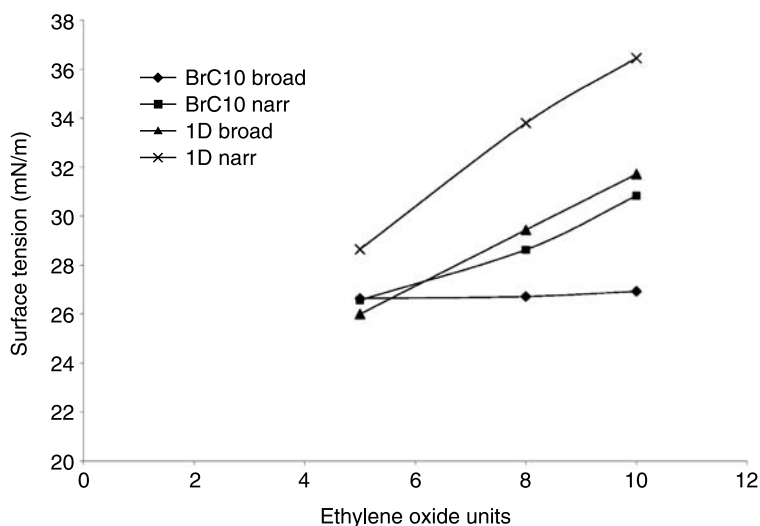


FIGURE 5.11 Surface tension at the critical micelle concentration as a function of the average number of ethylene oxide units.

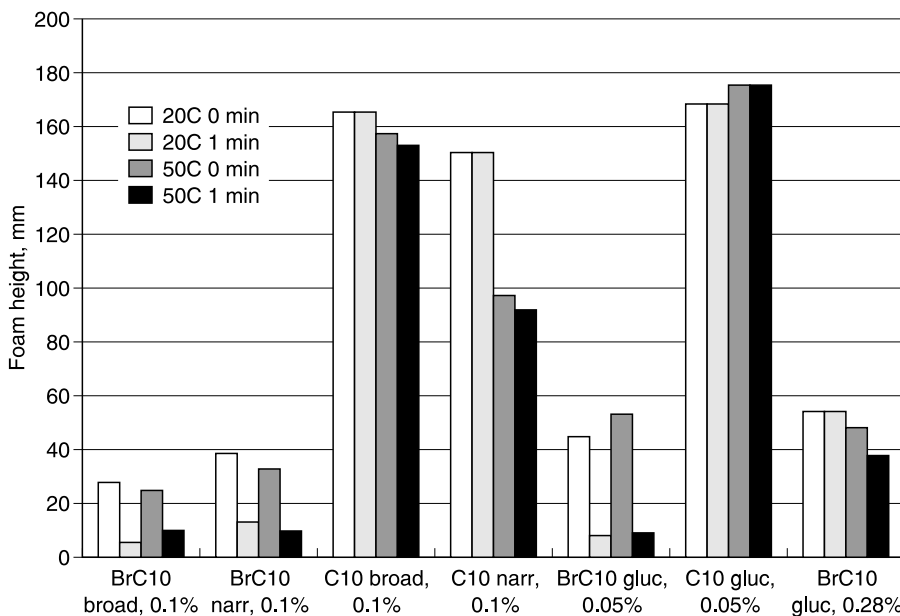


FIGURE 5.12 Foam height, winding equipment, for different C10 alcohols with 5 EO compared to alkyl glucosides from the same alcohols, immediately and after 1 min, at 20 °C and 50 °C.

Temperature effects are seen in one case, C10 narrow range, where the higher temperature gives lower foam depending on the solution having reached its cloud point at 50 °C.

5.3.1.2.3 At Hydrophobic Surfaces

5.3.1.2.3.1 Contact Angles

The change of the contact angle of a droplet of 0.25% surfactant solution on Parafilm® (as a hydrophobic model surface) was followed with time with a high speed video camera. The values after 60 sec are shown in Figure 5.13 versus amounts of EO (m).

Narrow range 1-decanol based surfactants show a larger contact angle than similar Guerbet C10 alcohol based surfactants. This observation corroborates well with the observed trend in the surface tension at the CMC. It is also in line with the fact that the contact angle of neat C10 Guerbet alcohol on Parafilm® is smaller than the contact angle of neat 1-decanol.

Broad range surfactants show smaller contact angles than similar narrow range surfactants, which again can be explained by the adsorption being tighter at the air–water interface.

5.3.1.3 Conclusions Overall

Technical ethoxylates from Guerbet C10 alcohol compared to straight chain decanol have the following properties:

- They contain higher amounts of unreacted alcohol
- They have higher critical micelle concentrations
- They have larger areas per molecule at the air–water interface

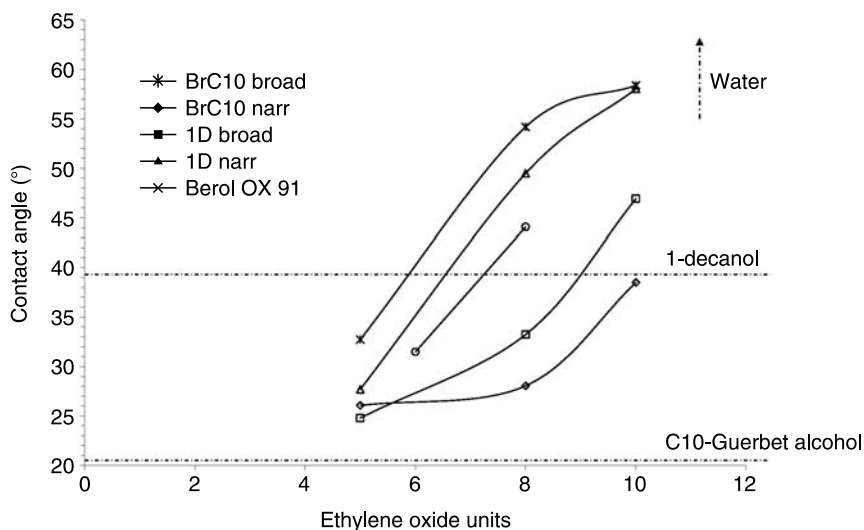


FIGURE 5.13 Contact angle (θ) on Parafilm[®] (60 s after drop formation) as a function of the average number of ethylene oxide units ($\langle m \rangle$) of 0.25 w% solutions of alcohol ethoxylates with $\langle m \rangle \geq 5$ ($T = 21 \pm 1^\circ\text{C}$, $45 \pm 10\%$ rH).

However, they also have:

- Lower surface tension
- Lower cloud points
- Less foam
- Lower contact angle against hydrophobic surfaces
- Lower inversion points in emulsion systems

With the simple automatic titration technique described above the ratio of hydrophobic co-surfactant to total surfactant (α) necessary to invert an emulsion from O/W to W/O can be obtained and related to other characterization methods like HLB. However, it refers to a specific system of oil, temperature, stirring rate etc. In this respect it is more similar to the PIT launched by Shinoda (3) or SAD emanating from Wadle (4).

The deviating behavior of the branched structures giving rise to an expanded area per molecule at the interface and yet a lower surface tension and smaller contact angle is not revealed by titration. To understand structure–property relationships at the molecular level complementary measurements of physicochemical properties need to be done. Titration shows the behavior of the actual technical mixture and is thus also useful for optimizing blends for specific purposes.

5.3.2 COMPARISON BETWEEN SOLVESSO 150 D AND METHYL LAURATE

With the same titration procedure as described above an investigation was made to fine tune the balance between two emulsifiers of different HLBs when the oil to be emulsified was changed from an aromatic solvent, Solvesso 150 D, to methyl laurate (model oils for an agrochemical formulation) due to environmental reasons.

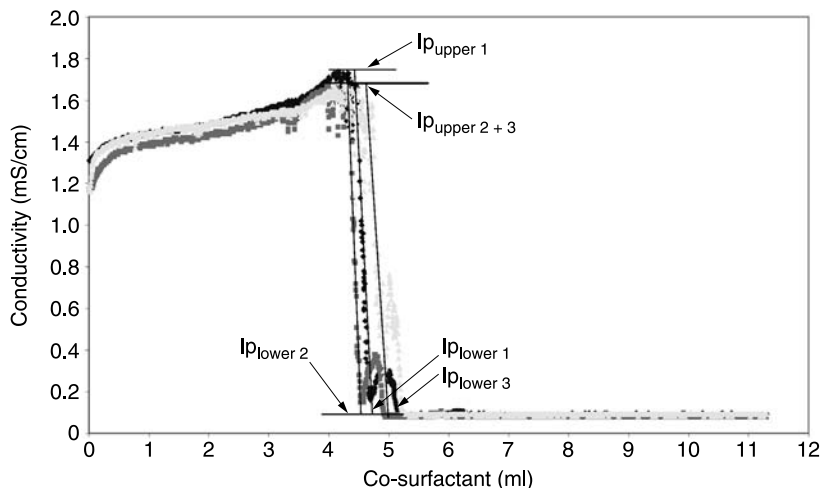


FIGURE 5.14 Conductivity as a function of the amount of added co-surfactant in the system of Berol 992/Solvesso 150 ND/water/NaCl/Berol 822 (Titration speed 4.44 $\mu\text{l/s}$).

As emulsifiers an alkoxyated short chain fatty alcohol (Berol 992) as the hydrophilic part and dodecyl benzene calcium sulfonate (Berol 822) as the hydrophobic part were chosen. The Scanalys[®] MPS-I system was used throughout the whole investigation. The measurements were made with a starting concentration of 6% Berol 992, to be closer to the emulsion system used in practice. The stirring speed was 300 rpm. Through the construction of the stirrer information about the rheology of the solution can be obtained. An additional magnetic stirrer at the bottom of the vessel was used.

With this emulsifier/oil system more fine structure was observed in the conductivity curves. The inversion remained clearly visible and the upper and lower inversion points could be deduced in the same way as before.

A typical run is shown in Figure 5.14 where Berol 822 is added slowly under stirring to the 50/50 Solvesso 150 D/water emulsion (25 °C). A very clear inversion is seen and the upper and lower inversion points can be determined. The average is taken as the inversion point. Three repetitive runs give smaller deviations but the fine structure and the inversion are reproducible within an uncertainty limit ($\pm 1.5\%$ for the percent co-surfactant of the total surfactant). A series of tests with increasing amounts of methyl laurate, from 0 to 100% of the oil phase, was made. The results are shown in Figure 5.15.

As can be seen in the graph, more of the hydrophobic co-surfactant is needed when methyl laurate is used as the oil phase. Methyl laurate could then be described as more “hydrophobic” than the aromatic solvent, i.e., having a higher equivalent hydrocarbon number (EACN) (10). Approximate values for EACN for the two oils used here are around 3–4 for the aromatic solvent and for methyl laurate around 7 (by analogy with ethyl oleate) (11), which is consistent with the results in this investigation. It is well known that aromatic oils have a tendency to penetrate into the interfacial layer (12) thus changing its curvature. One could anticipate that this would happen here, thus decreasing the demand for a hydrophobic co-surfactant to achieve the balanced state for the aromatic oil.

It has been shown (13) that when mixtures of oils with very different polarity, like hexadecane (ACN = 16) and ethyl oleate (EACN = 6–7), are used there is an interfacial segregation of the oils

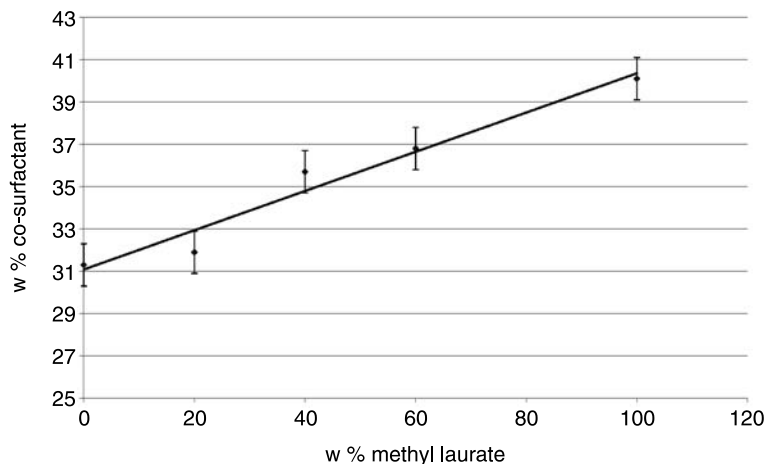


FIGURE 5.15 Inversion point dependence on weight percent of methyl laurate in the oil mixture for the emulsifier system Berol 992 and Berol 822.

causing an increased concentration of the most polar oil close to the interfacial layer. The results in this case do not indicate any such segregation but rather show that the stepwise increased ratio also causes a stepwise increase of hydrophobicity. Successive measurements with mixtures of solvents and titrations with known emulsifier pairs can obviously be used to classify and describe the balance of a practical emulsion system.

As has been pointed out in the introduction, the surfactant ratio at the inversion point is the point of minimal interfacial tension, i.e., where the formation of droplets is easiest, but it is also the most unstable emulsion situation (14). To find the stable area, tests have to be made at some distance from the inversion point. These studies are of course easier and more practical once the location of the inversion point is known.

5.3.3 OPTIMIZATION OF A SURFACTANT COMBINATION FOR SOIL REMEDIATION

An application where the minimal interfacial tension is the optimum situation is soil remediation (15). The last example is taken from development work for that application.

To clean up contaminated soil different techniques can be applied. One of the most efficient is surfactant flushing, where surfactants are used to facilitate the transport of water insoluble contaminants like fuels, solvents, or halogenated hydrocarbons out of the ground. It is very important to find the lowest interfacial tension, i.e., to be within the microemulsion region (Winsor III) to obtain the best results. When balancing the surfactant system the oil phase can either be the dirt as such or a model oily dirt with similar properties.

In the example given here Danish winter diesel is the oil phase and the emulsifiers are a hydrophilic alkyl glucoside based on a 50/50 C8/C10 alcohol mixture (AG 6210), and a hydrophobic nonionic, C11E2 (Berol 532). When investigated in the system described in Section 5.3.1 the hydrophilicity of AG 6210 was very similar to pure straight chain C10 glucoside.

In this case the procedure was reversed as compared to the examples in Sections 5.3.1 and 5.3.2, starting with the hydrophobic surfactant, C11E2, in an oil/water 50/50 mixture and titrating in the hydrophilic surfactant until conductivity started to increase. The fine structure in the graph showing conductivity versus surfactant concentration was compared to the equilibrium behavior

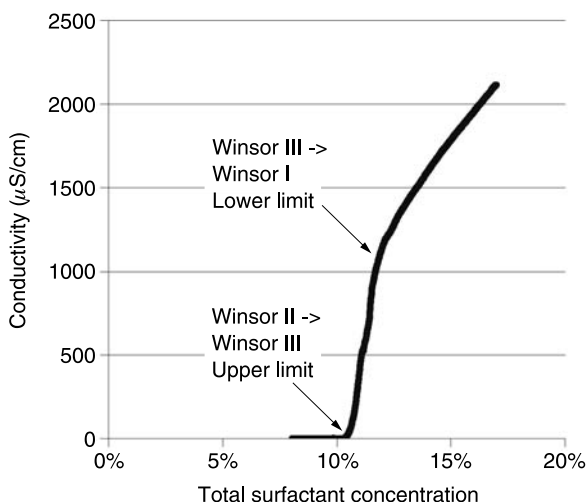


FIGURE 5.16 Breakpoints in the conductivity scan for Danish diesel/water 50/50, with C11E2 as starting emulsifier and C8–10 glucosides added as cosurfactant against total amount of surfactant.

of corresponding samples. In this case two bends in the curve were seen and found to correspond to the upper and lower limits of the Kahlweit fish body in the phase diagram. The analysis uses the well known terms from microemulsion studies (16), Winsor I, II, and III, to describe whether the surfactant phase is in the water phase, in the oil phase, or in the three-phase region.

Figure 5.16 shows a typical run with upper and lower limits marked and what they correspond to in an equilibrium system. A series of titrations with different starting concentrations was made and the resulting bends in the curve were related to the phase diagram as is seen in Figure 5.17.

To confirm that we had found the optimum situation with minimal interfacial tension the interfacial tension was measured between oil and water phase with 8% total surfactant and the part of the hydrophobic surfactant being varied from 0 to 0.9 (Figure 5.18). The minimum was found at 0.7 which corresponds well with the titration results and the phase diagram shown in Figure 5.17.

Later investigations on sand columns on a laboratory scale as well as pilot scale trials have confirmed the efficiency of the mixture investigated here as surfactants for flushing in soil remediation.

5.4 CONCLUSIONS

In this chapter various methods of using emulsion inversion as a technique for characterizing and fine tuning surfactant formulations have been discussed. The phenomenon, as such, with the inversion point being related to the minimum in interfacial tension and interfacial curvature equal to zero, is well known and applied in many areas (1,17,18). To know where your formulation is situated in the phase diagram, and especially the location of the optimum formulation with $SAD = 0$, is crucial for efficient and qualified product development. The tool described here opens a way for automatic HLB scanning and thus easy access to this important information. Examples have been given on how to characterize and compare surfactants of varying structures when they are used in similar surroundings. Effects of varying the surroundings, such as the

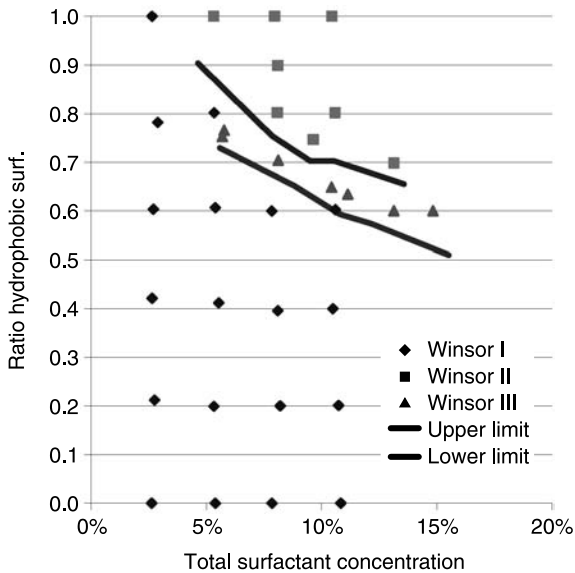


FIGURE 5.17 Conductivity scan together with equilibrium results for Danish diesel/water 50/50, with C11E2 and C8–10 glucoside as emulsifiers.

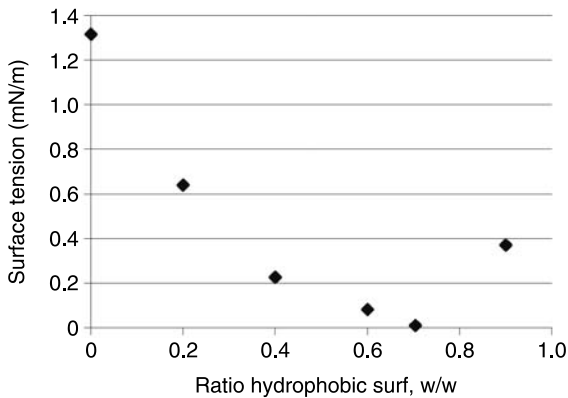


FIGURE 5.18 Interfacial tension dependence on emulsifier mixture for Danish diesel and water.

character of the oil, have been shown as well as optimization of surfactant mixtures for use in specific applications like soil remediation.

More work on other possible ways of performing the titration needs to be done to facilitate the interpretation of the inversion results in terms of phase behavior. Extensive comparisons with equilibrium samples will give access to explanations for fine structures in the titration curves and thus increase the feasibility of this technique. All in all we hope to see an increase in application of the principles underlying the results in this study as well as an increased usage of the equipment in development of new products and formulations for novel as well as established application areas.

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