

## ABOUT CHARACTERIZATION OF SURFACTANTS OUTSIDE THE HLB-SYSTEM

Ingegard Johansson, Akzo Nobel Surface Chemistry AB, Sweden  
Ilja Voets, Wageningen University and Research Center, The Netherlands

### ABSTRACT

In our work with new surfactants, having structures that are not easily treated with the Griffin or Davies HLB formulas, a need for characterization that would work for all kinds of structures has come up. In this paper a possible system is discussed using a titration method in an emulsion system to find the phase inversion, i.e. how far the structure of a specific surfactant is from forming aggregates having a spontaneous curvature of zero.

In essence, the investigation can be characterized as a way of making an HLB scan using a mixture of oil, water and surfactant and register the response to a continuous slow addition of a co-surfactant. The easiest response to measure is the conductivity of the stirred mixture, which reveals when the mixture switches from an oil-continuous to a water-continuous emulsion or vice versa depending on the starting point.

We have studied a model system of nonionic surfactants with straight and branched hydrophobes as well as broad and narrow range ethylene oxide distribution in the hydrophilic part. The co-surfactant has been Span® 80, a hydrophobic oleyl monoglyceride. Attempts were thus made to relate the conventional HLB:s to the data measured and to assign relative HLB:s to for instance the surfactants with branched hydrophobes. Cloud points, CMC, surface tension, wetting, interfacial tension, foam and other functional properties were measured and the co-variation of these data has been analyzed. The system was stretched to cover also other surfactant types, for instance the sugar based nonionics

From the titration the following conclusions could be drawn.

- The broad range ethoxylates are less hydrophobic than the narrow range ones.
- The ethoxylates with > 3EO:s made from branched hydrophobes require less co-surfactant, i.e. act as more hydrophobic, than those with a straight chain in an emulsion from decane/water 50/50. This can be understood from the bulkiness of the hydrophobe making the form of the surfactant closer to a cylinder i.e. having a Critical Packing Parameter closer to 1, thus needing less hydrophobic additive to come to a zero curvature of the interface.
- Alkyl glucosides made from the same fatty alcohols show the same difference between the straight and branched structures but to a larger extent.
- Comparing the EO-hydrophile with the glucosidic hydrophile does not give an unambiguous correspondence but depends on the balance in the molecular mixture. Both glucosides contain the same average amount of glucose, 1.6, per hydrophobe. For the straight chain the glucosidic part corresponds approximately to 7 EO:s (isomerically pure) but for the branched C10 it is more similar to 5 EO:s (narrow range).

### INTRODUCTION

When oil and water are mixed, an emulsion is formed. In many applications the simultaneous presence of a polar and an unpolar solvent is desirable. The resulting emulsion often needs to be stable. This stability is achieved by the addition of one or several emulsifiers. The problem of choosing the best system for this purpose is ubiquitous. Solutions have been sought in describing the structure of the emulsifier in terms of HLB, Hydrophilic-Lipophilic Balance (1), or CPP, Critical Packing Parameter (2). These attempts have not taken into account the influence of oil, temperature, salt etc which play important roles for emulsion stability. Shinoda (3) works with temperature effects and uses PIT (phase inversion temperature) 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, that is heated or cooled past the phase inversion temperature, is that it changes its morphology. i.e. inverts by going from an O/W to a W/O emulsion or vice versa. Expressed in another way this means that the spontaneous curvature,  $H_0$ , of the interfacial film changes sign and passes a flat form where  $H_0 = 0$ . This point is the balanced point or optimal point where a bicontinuous microemulsion is formed and the interfacial tension is at its minimum.

Davies writes “ The spontaneous mean curvature  $H_0$ , 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 to decide 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 nineties.

It has also been shown by Salager et al (6) that the most stable emulsions are to be found at a specific distance from the balanced situation of  $H_0 = 0$ , or in his terminology,  $SAD = 0$  (surfactant affinity difference).

Thus it is important to find this balanced point for the actual emulsion or formulation that you are optimizing.

The aim of the work reported here is to find a practical way of deciding the balanced or optimal point for a mixture that can be practiced with all types of emulsifiers, also the ones that don't react to temperature or salt. An automatic titration procedure is used by which a co-surfactant is added to an oil-water-surfactant blend under stirring at constant temperature. The morphology changes of the emulsion is followed with conductivity which suddenly goes to zero when the emulsion inverts from O/W to W/O. By using reference compounds like isomerically pure ethoxylates and the same co-surfactant and oil the behavior of any other surfactant can be compared to systems with known HLB:s or whatever traditional description concepts that are familiar to the user.

Series of C10 nonionics with branched or straight hydrophobe and broad or narrow ethylene oxide distribution or glucose as hydrophile, have been studied and compared. Physico-chemical data as well as Optimal balance with the titration method have been decided. As co-surfactant Span 80®, oleyl monoglyceride, has been used.

## EXPERIMENTAL

Products:

Lab. products from Akzo Nobel Surface Chemistry AB:

Guerbet C10 alcohol with 3, 5, 8 and 10 ethylene oxide units, both narrow and broad range distribution

Straight C10 alcohol with 3, 5, 8 and 10 ethylene oxide units, both narrow and broad range distribution

Glucosides from the same two alcohols with an average degree of polymerization of 1.6

Commercial products from Akzo Nobel Surface Chemistry AB: Berol ox 91-6 and 91-8 which are C9-11 alcohol with 6 or 8 ethylene oxide units, broad range.

Isomerically pure  $C_{10}E_5$ ,  $C_{10}E_7$ ,  $C_{10}E_8$  from Sigma Aldrich and Fluka.

Span® 80, oleyl monoglyceride, from Fluka, n-decane (>95%) from Merck. Water was distilled and de-ionized.

Critical Micelle Concentration.

Surface tension was measured on a KSV unit with a Sigma 70 program using the Du Nouÿ ring method.

Contact angles.

The contact angle was measured on Parafilm® with a FTÅ200 instrument in a climate controlled room ( $T=21\pm 1^\circ\text{C}$ ,  $45 \pm 10\%rH$ ).

Cloud points.

Mixtures of 1.0w% surfactant in distilled water, aqueous NaCl (2.0g/l; 0.034M) 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.

#### Foam

The foam height is 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 one minute. The foam height is recorded immediately and after 1 min.

#### Conductivity measurements.

N-decane (24.25g; 0.15mole), aqueous NaCl (24.25g; 2g NaCl/l; 0.034M) and surfactant (1.50g) were homogenized in a thermostated glass vessel. Temperatures at the inversion point were in the region  $24.6^{\circ}\text{C} \leq T \leq 26.3^{\circ}\text{C}$ . 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  $>15000\text{rpm}$  (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 0.15ml/min. This mixture will be referred to as 'cosurfactant'. Figure 11 shows the experimental setup of the automatic titration technique.

Some measurements were performed on the Scanalys® equipment. It is essentially the same experimental setup ([www.scanalys.com](http://www.scanalys.com)), but one single stirrer with built-in electrode was used at 225 and 300 rpm. The Span® 80/n-decane (8/3 w/w) was titrated in with a dosing rate of 4.44\_l/s.

## RESULTS AND DISCUSSION

### Physico-chemical measurements.

#### Distributions.

Typical ethylene oxide distributions for  $\text{C}_{10}\text{E}_5\text{s}$  are shown in Figures 1 and 2. It should be noted that there is a general difference in distribution between the two alcohols due to the sterically crowded structure of the branched decyl alcohol. This gives rise to more starting material being left in the ethoxylated product which influences the distribution of the different parts in the mixture between the oil and the water phase and thus the physico-chemical behavior.

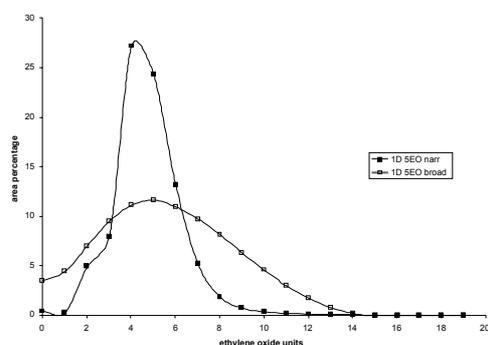


FIGURE 1. Ethylene oxide distributions of decyl alcohol ethoxylates, broad and narrow.

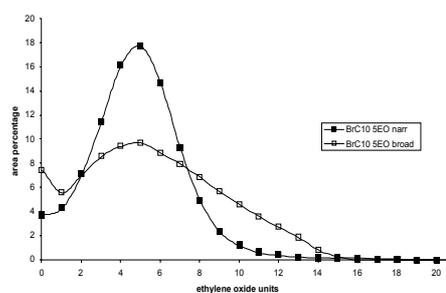


FIGURE 2. Ethylene oxide distributions of branched decyl alcohol ethoxylates, broad and narrow.

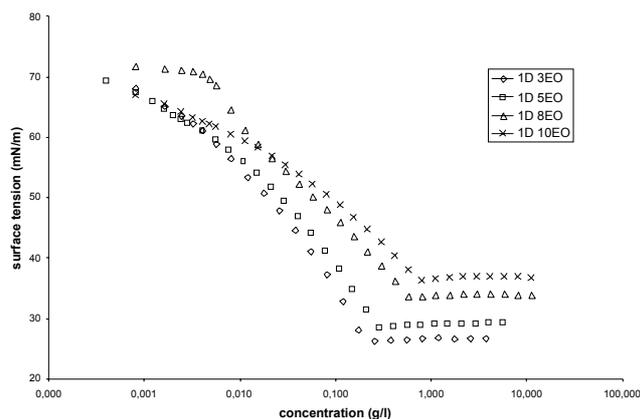


FIGURE 3. Surface tension as a function of surfactant concentration of narrow range 1-decanol ethoxylates ( $T=21\pm 1^\circ\text{C}$ ).

### CMC.

In Figure 3 typical CMC curves are given for the narrow range n-decyl alcohol series. In the case of  $\text{C}_{10}\text{E}_3$  not the whole product mixture is dissolved, which means that the value of the CMC refers to a part of the mixture and is not valid. It is consequently not included in the CMC discussion below.

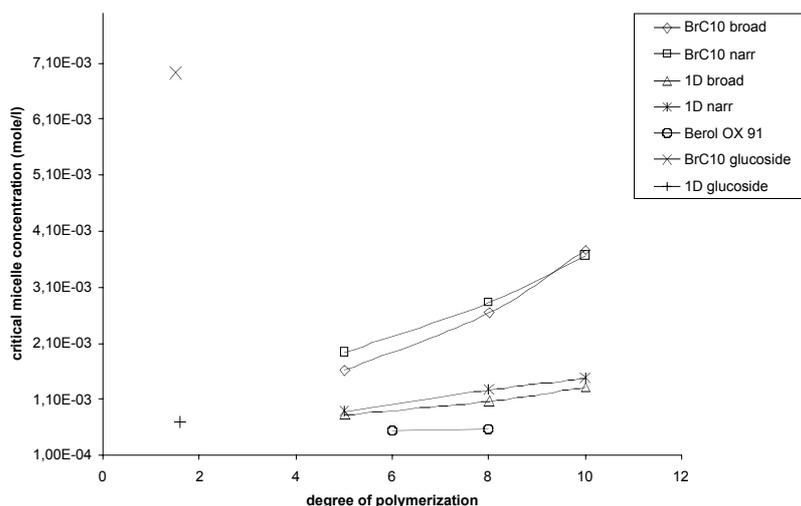


FIGURE 4. Critical micelle concentrations of technical grade alcohol ethoxylates and alkyl polyglucosides as a function of degree of polymerization of the head group ( $T=21\pm 1^\circ\text{C}$ ).

In Figure 4 the dependence of the CMC:s on the chemical structures is shown. As expected (7), the CMC increases for the same type of surfactant with 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 CMC:s 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 homologues 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 CMC:s than the pure C10 types due to the heterodispersity of the hydrophobe, again giving more freedom in packing the different homologues into the micelles.

The glucosides show a huge difference between the two alcohols, again with a much higher CMC for the branched product. It is well known that the hydrophilic/lipophilic balance of the alkyl glucosides is even more sensitive to changes in the length of the hydrophobic chain than that of the ethoxylates (8).

#### Area per molecule at the air/water interface

Some further information can be extrapolated from the surface tension versus log concentration plots. The area per molecule ( $a_0$ ) at the air/water interface as a function of  $\langle m \rangle$  is shown in Figure 5.

Clearly,  $a_0$  increased 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.

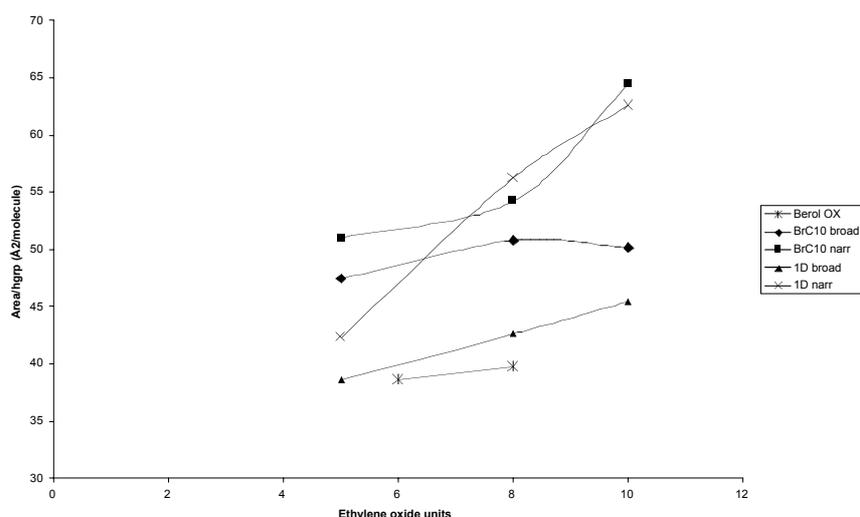


FIGURE 5. Area per molecule at the air/water interface as a function of the average number of ethylene oxide units

Both branching of the hydrophobe and broadening of the EO distribution had an influence on the adsorption. Surfactants with the same type of hydrophobe showed similar area per molecule at the air/water interface for small head groups. Surfactants with the same type of ethylene oxide distribution showed similar  $a_0$  values for bigger head groups. Thus the influence of the hydrophobe was dominating for smaller head groups and the hetero dispersity of the EO chain was the dominant factor for larger head groups. This reflects the increase in the size of the head group relative to the hydrophobe with increasing  $\langle m \rangle$ . Because branched C10 hydrophobes are bulkier than straight C10 hydrophobes, branching had an adverse effect on the adsorption at the air-water interface. It is obvious that broad range surfactants had smaller areas per molecule than narrow range surfactants. Most probably this is a result of the packing advantages of a broader EO distribution.

#### Surface tension at CMC

Another information to be gained from the CMC curves is the surface tension at or above CMC, see Figure 6.

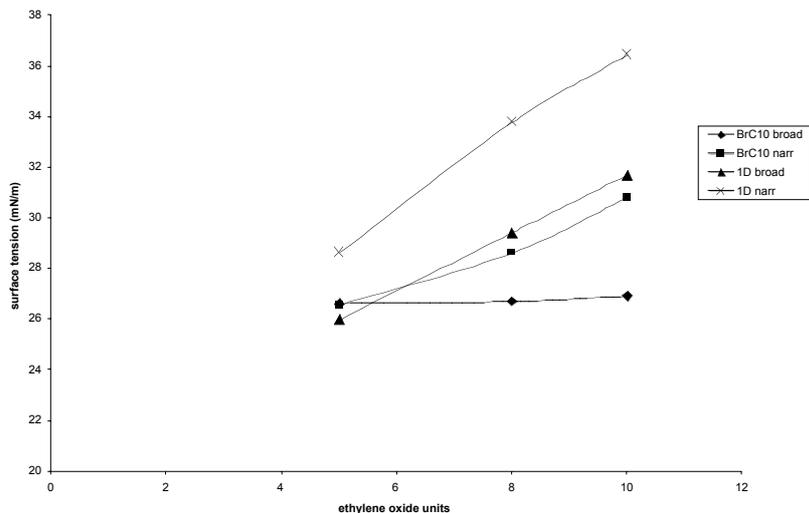


FIGURE 6. Surface tension at the critical micelle concentration as a function of the average number of ethylene oxide units.

Surface tension increased with increasing  $\langle m \rangle$  (except for the broad range Guerbet alcohol based compounds). For the same type of surfactant, the smaller the head group, the more surfactant adsorbs at the interface, and the lower the surface tension. Note also that the same inconsistency is found for the branched C10 broad range compounds in the area/molecule graph.

The Guerbet alcohol based surfactants showed 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. One plausible explanation is the following. The branch may be positioned planar to the interface, while the rest of the surfactant tails is positioned lateral to the interface. Therefore, the branch reduces the contact between water and air resulting in lower surface tensions for branched surfactants. However surfactant anchoring/geometry at the interface is possibly not (most) important in this respect, as the surface tension of neat Guerbet C10 alcohol is by itself lower than that of 1-decanol (as is the contact angle on Parafilm®).

### 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 s are shown in Figure 7 versus amounts of EO.

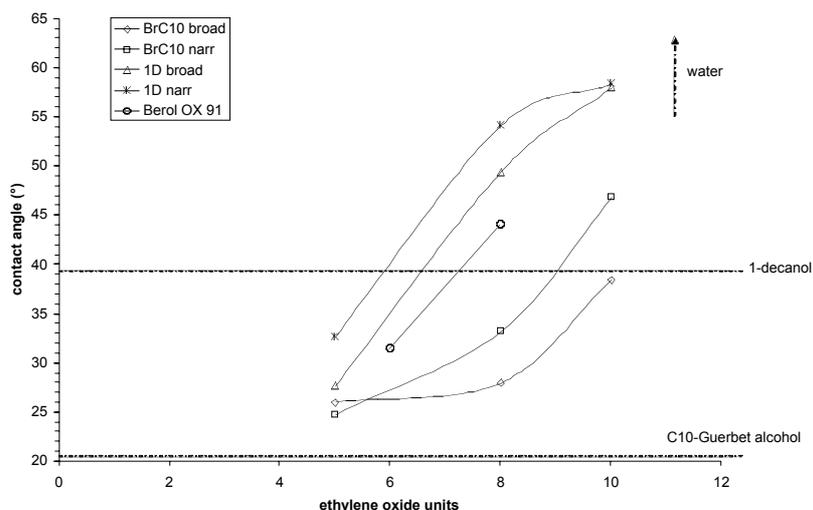


FIGURE 7. Contact angle ( $\theta$ ) on Parafilm® (60s after drop formation) as a function of the average number of ethylene oxide units ( $\langle m \rangle$ ) of 0.25w% solutions of alcohol ethoxylates with  $\langle m \rangle \geq 5$  ( $T=21 \pm 1^\circ\text{C}$ ,  $45 \pm 10\%rH$ ).

Narrow range 1-decanol based surfactants showed 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 showed smaller contact angles than similar narrow range surfactants, which again can be explained by the adsorption being tighter at the air-water interface.

### Cloud points

To fit the cloud points of all surfactants studied in this work into the experimental window, cloud points in 11% BDG (Figure 8) were determined.

Cloud points increase with increasing average EO chain length. As the head groups are at the micellar surface, micelles with larger head groups will appear more hydrophilic. Moreover, steric repulsion between the micelles will increase with increasing size of the head group.

Branched surfactants are less tightly packed in micelles. Therefore there is less steric repulsion between the micelles and the branched surfactants form a separate surfactant phase earlier. Another possible explanation is the formation of a different shape and size of micelles for branched surfactants. These aggregates might have stronger intermicellar attractive forces resulting in lower cloud points.

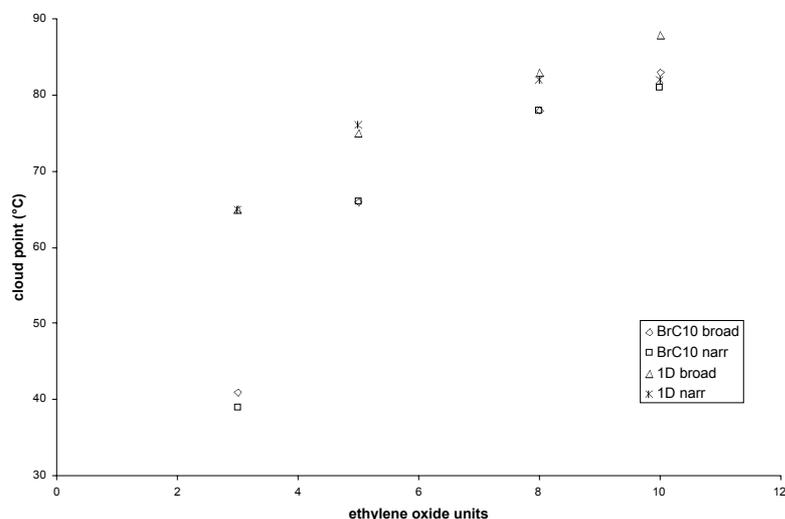


FIGURE 8. Cloud point (CP) as a function of the average number of ethylene oxide units  $\langle m \rangle$  of 1.0w% solutions of alcohol ethoxylates with  $\langle m \rangle \geq 5$  in 11% butyl diethylene glycol.

### Foam

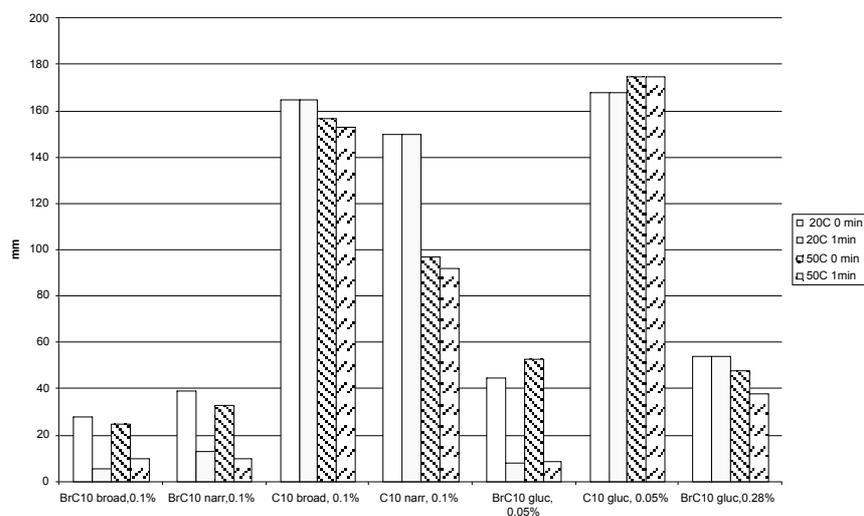


FIGURE 9. Foam height, winding equipment, for different C10 alcohols with 5 EO compared to alkyl glucosides from the same alcohols, immediately and after 1 min, at 20 °C and 50 °C.

The foam was measured for the different C<sub>10</sub>E<sub>5</sub>s and the corresponding glucosides, see Figure 9. 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. Temperature effects are seen in one case, C10 narrow range, where the higher temperature gives lower foam depending on that the solution has reached its cloud point at 50 °C.

### Conclusions of the physico-chemical measurements

Branching of the hydrophobe

- Increases CMC
- Increases area per head group

But

- Decreases surface tension
- Decreases contact angle
- Decreases cloud point
- Decreases foam.

### Inversion points of emulsions, titration of co-surfactant.

Some of the conclusions of the preceding session are counter intuitive, like higher CMC (indicating more hydrophilic compounds) and at the same time lower surface tension and contact angles (more hydrophobic compounds).

By finding out how far each surfactant mixture is from creating a spontaneous curvature equal to zero in a 50/50 oil water emulsion we may be able to describe the behavior in the interface better .

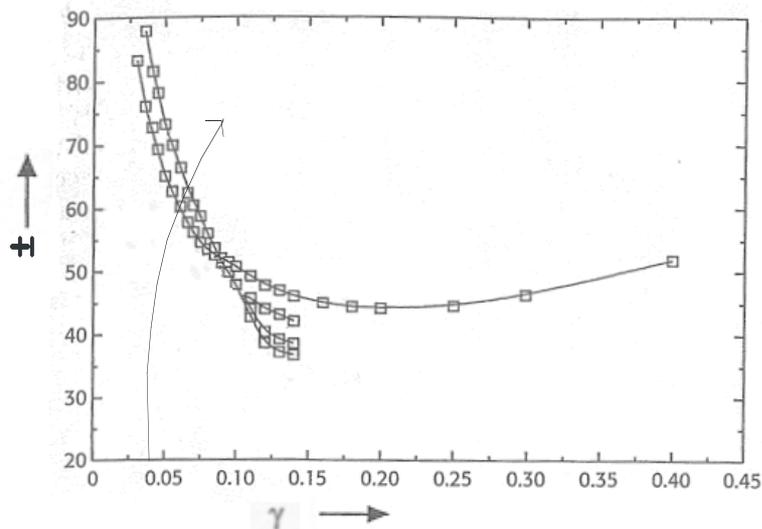


FIGURE 10. Schematic representation of a typical titration path (arrow) during the conductivity scan with the automatic titration technique,  $\alpha$  = co-surfactant/total surfactant concentration (w%),  $\gamma$  = total surfactant concentration (w%).

This is done via a titration procedure that was described earlier. How the titration moves the system over the oil/water/surfactant phase diagram, keeping the oil/water ratio constant at 50/50 is shown in Figure 10. By adding a co-surfactant the total surfactant concentration increases somewhat and the ratio between the two changes towards a more and more hydrophobic surfactant mixture, until it balances to a planar structure and then flips over changing the nature of the emulsion from being water continuous to being oil continuous.

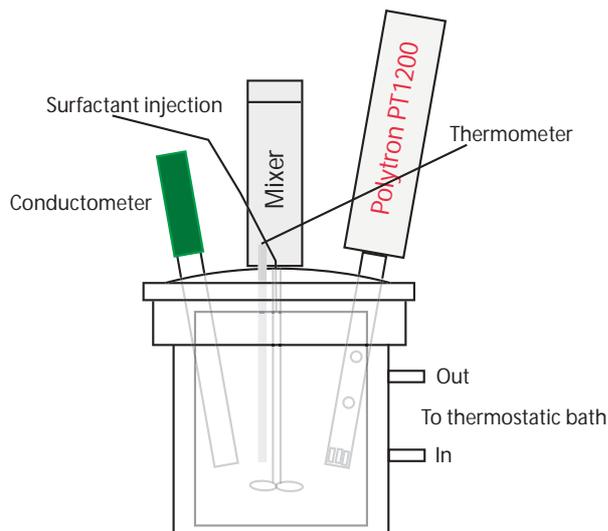


FIGURE 11. Experimental set-up for the co-surfactant titration followed with conductometry. Commercially available as the Multi Parameter Scanning (MPS) instrument from Scanalys, ([www.scanalys.com](http://www.scanalys.com)), with possibilities to measure turbidity, pH, conductometry and viscosity simultaneously

Figure 11 shows the experimental set-up and Figure 12 a typical conductivity scan with conductivity against added co-surfactant, Span80 in ml.

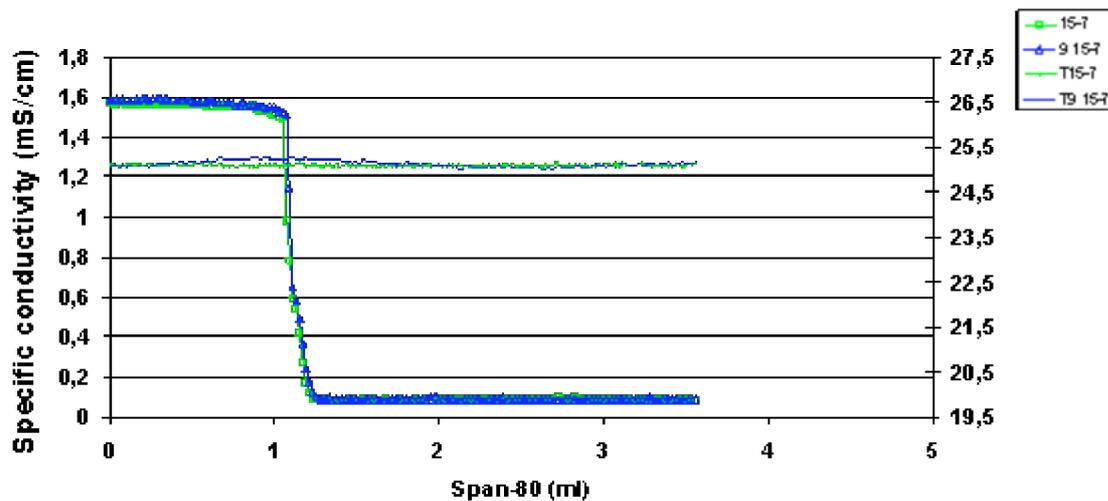


FIGURE 12. Conductivity scan for  $C_{10}E_3$  broad range with Span-80/n-decane/NaCl/water.

This is then evaluated and recalculated to find the upper and the lower inversion points (IP) according to the procedure described in Figure 13.

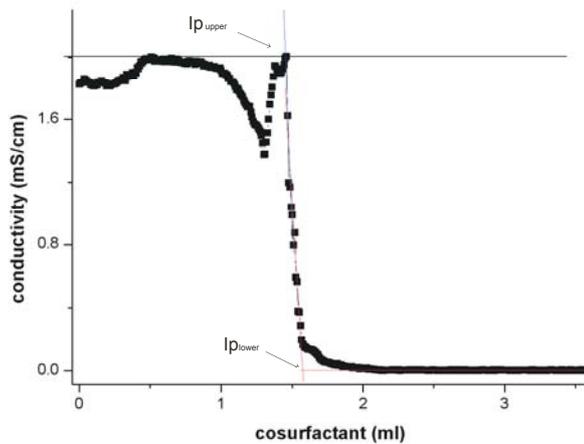


FIGURE 13. : Linear fits to the first and last part of the steep conductivity drop in a plot of conductivity as a function of the amount of added cosurfactant in a pseudo quinary SOW system of 1-decyl glucoside/n-decane/water/NaCl/Span® 80 ( $T=25^{\circ}\text{C}$ ,  $dr=0.15\text{ml/min}$ ,  $ss>15000\text{rpm}$ ) are shown.  $IP_{upper}$  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 conductivity.  $IP_{lower}$  is the amount of added 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

In Figure 14 all the the inversion points for the four series of ethoxylated surfactants, the isomerically pure ones and the alkyl glucosides are gathered in terms of w % of Span80 of the total surfactant package against degree of polymerization.

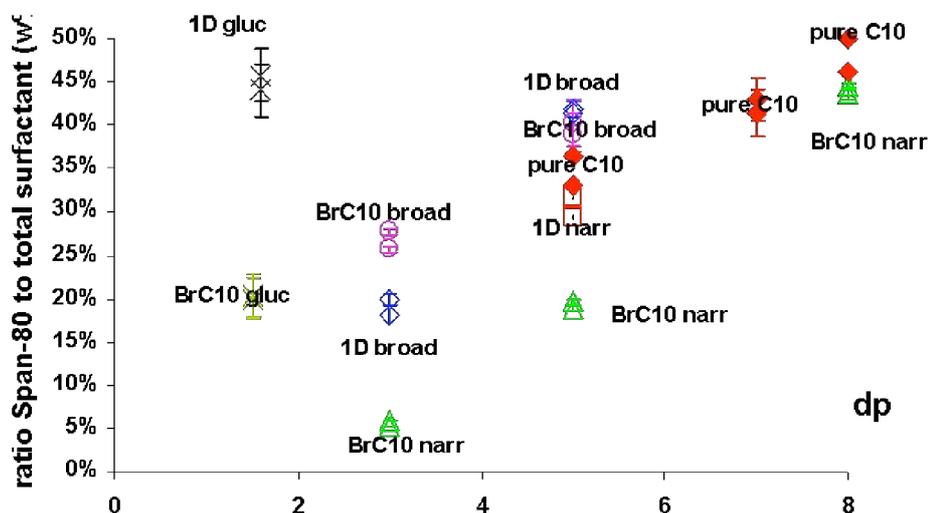


FIGURE 14. Inversion points ( $IP_{upper}$  and  $IP_{lower}$ ) as a function of the degree of polymerization of technical grade alcohol ethoxylates, technical grade alkyl glucosides and isomerically pure alcohol ethoxylates with 5, 7 or 8 EO units. Error bars indicate the deviation of two individual measurements on the system from the average value.

Results from the titration indicate:

- The broad range ethoxylates are less hydrophobic than the narrow range ones.
- The ethoxylates with  $> 3\text{EO:s}$  made from branched hydrophobes require less co-surfactant, i.e. act as more hydrophobic, than those with a straight chain. This can be understood from the bulkiness of the hydrophobe making the form of the surfactant closer to a cylinder i.e.

having a Critical Packing Parameter closer to 1, thus needing less hydrophobic additive to come to a zero curvature of the interface.

- Alkyl glucosides made from the same fatty alcohols show the same difference between the straight and branched structures but to a larger extent.
- Comparing the EO-hydrophile with the glucosidic hydrophile does not give an unambiguous correspondence but depends on the balance in the molecular mixture. Both glucosides contain the same average amount of glucose, 1.6, per hydrophobe. For the straight chain the glucosidic part corresponds approximately to 7 EO:s (isomerically pure) but for the branched C10 it is more similar to 5 EO:s (narrow range).

Finally the average of the inversion point values is taken as the inversion point and used for a tentative coordination of an Equivalent HLB value comparing with the results for the isomerically pure C<sub>10</sub>E<sub>5</sub>, C<sub>10</sub>E<sub>7</sub> and C<sub>10</sub>E<sub>8</sub>, for which the HLB:s can be calculated according to Griffin, see Figure 15.

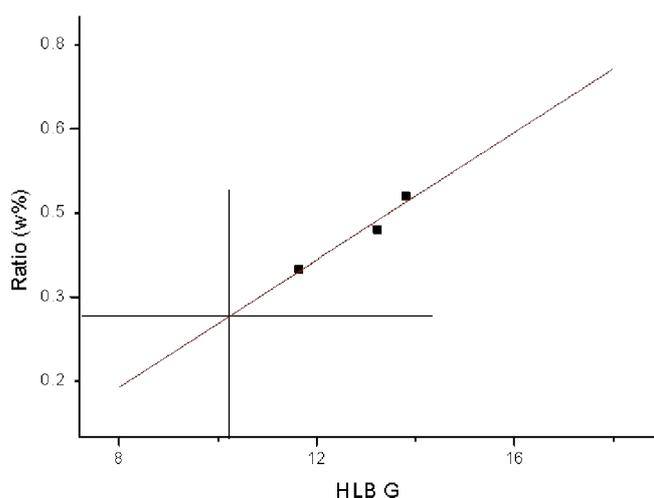


FIGURE 15. : Extrapolation of a linear fit on the inversion points (average of upper and lower) as a function of the HLB number (Griffin) of pure C<sub>10</sub>E<sub>m</sub> alcohol ethoxylates is shown. The equation obtained in this manner provides a way to determine the Equivalent HLB number of any (mixture of) surfactant(s) once its inversion point in the same system (i.e. the same temperature, pressure, type of oil) is established.

## Conclusions overall

Technical grade C<sub>10</sub>E<sub><m></sub> surfactants are blends of surfactant homologues with an average length of the EO distribution at <m>. Depending on catalyst the distribution of homologues can be made more or less narrow.

Broad range surfactants show:

- higher amounts of unreacted alcohol
- higher critical micelle concentrations
- smaller areas per molecule at the air/water interface
- lower surface tension
- lower contact angles
- higher cloud points
- higher inversion points

The behavior of technical grade C<sub>10</sub>E<sub><m></sub> surfactants is shown to be dependent upon both the shape and mean of the EO distribution. It is also strongly dependent upon the surfactant environment. Therefore, it is not possible to universally classify broad range surfactants as more hydrophilic or hydrophobic than narrow range surfactants. It is not possible to determine an increment in (a factor describing the) hydrophilicity due to head group heterodispersity as the increment is dependent upon <m> and surfactant environment (i.e., emulsion or aqueous solution). This results from the fact that it is not possible to treat the surfactant blend as a pure surfactant with a number of EO units equal to

<m> (so called lumping). Selective adsorption, partitioning and phase separation of low and/or high homologues make lumping impossible.

Likewise, it is not possible to universally classify branched surfactants as more hydrophilic or hydrophobic than straight chain surfactants. Therefore, it is not possible to determine an increment in (a factor describing the) hydrophilicity due to branching as the increment is dependent upon <m> and surfactant environment (i.e., emulsion or aqueous solution).

Branched surfactants show:

- higher amounts of unreacted alcohol
- higher critical micelle concentrations
- larger areas per molecule at the air/water interface
- lower surface tension
- lower contact angle
- lower cloud points
- less foam
- lower inversion points

Guerbet branching of the hydrophobe results in both hydrophobic and hydrophilic shifts in surfactant behavior. This is partly due to the influence of the unreacted alcohol which decreases with increasing <m>. Moreover, the increased CPP due to Guerbet branching results in both hydrophilic shifts (higher CMC) and hydrophobic shifts (lower cloud point).

All studied alkyl polyglucosides and polyoxyethylene alkyl ethers spontaneously form O/W emulsions (3w% surfactant) in aqueous NaCl/n-decane ( $\lambda = 1.0$  by weight) except narrow range 1D 3EO (W/O emulsion). It is possible to invert emulsions with alkyl polyglucosides and  $C_{10}E_{<m>}$  for  $<m> \leq 8$  if the ratio of cosurfactant to (total) surfactant necessary for the inversion is not too high (approximately  $\leq 50\%$ ). Partitioning of surfactant homologues into the water and oil phases and surfactant geometry are the dominant factors that influence the position of the balanced point.

With a simple automatic titration technique the ratio of hydrophobic co-surfactant to total surfactant ( $\lambda$ ) necessary to invert an emulsion from O/W to W/O, can be obtained. The HLB numbers (Griffin) of isomerically pure straight alcohol ethoxylates were plotted as a function of ( $\lambda$ ). The equivalent HLB number (EHLB) of any (mixture of) surfactant(s) can be determined from this graph and the corresponding equation once  $\lambda$  is measured with the automatic titration technique. This method of surfactant classification is more precise and refers to a specific oil/water/temperature system which the HLB number does not. In this respect it is more similar to the HLB temperature concept launched by Shinoda (3).

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