Does hydrophobe branching make a surfactant more or less hydrophilic?

Dr Ingegard Johansson of **Akzo Nobel Surface Chemistry** explains the complex chemistry behind some new products

The hydrophobic-hydrophilic question came up in our search for new and efficient hydrophobic raw materials for surfactants. It was known that branching with defined branches like the Guerbet type gives good environmental properties, such as lower aquatic toxicity and easy biodegradation, and one would also expect it to lead to low foaming and good cleaning performance. However, a detailed structure-performance knowledge was lacking.

We carried out an investigation which filled in that gap and, with further fine-tuning, gave rise to a couple of new members of the Akzo Nobel product portfolio. An automatic titration technique was also developed for the characterisation of the surfactants and surfactant blends.

Physico-chemical studies

A series of non-ionic surfactants was synthesised, based on different straight-chain or Guerbet-branched decyl alcohols. The hydrophilic part was ethylene oxide (EO) or glucose. For the EO derivatives, the total amount of EO varied, as did the distribution, i.e. both broad and narrow. The glucosides were made with only one degree of polymerisation.

Many of their physico-chemical properties were determined and some results are given here. More detail was given in a paper at CESIO 2004 in Berlin.[1] As shown in Figure 1, the Critical Micelle Concentration (CMC) of the surfactants depends both on their branching and the type of distribution.

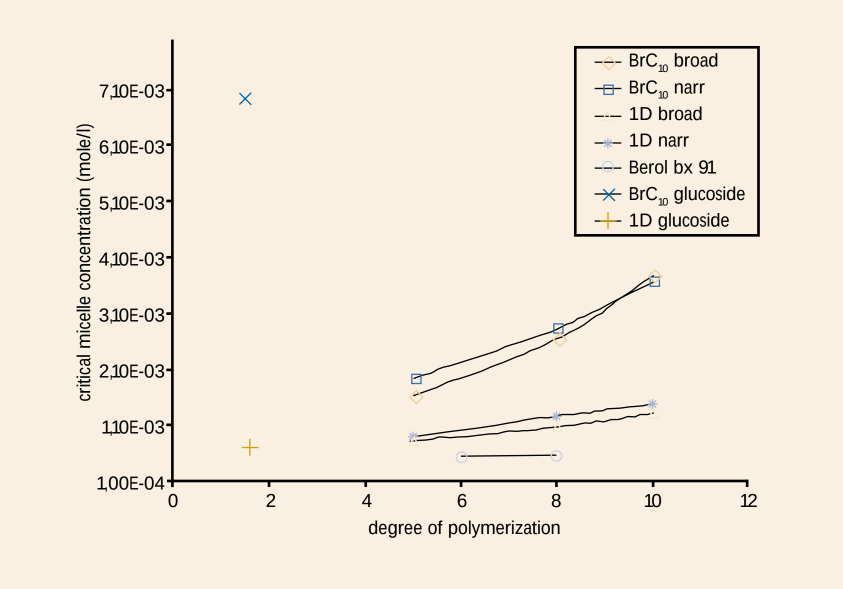

Figure 1- CMCs of technical grade alcohol ethoxylates & alkyl polyglucosides as a function of degree of polymerisation of the head group

Note: Temperature = 21±1°C. Br C_{10} broad/narrow- broad/narrow range ethoxylates of branched decyl alcohol, 1D broad/narr - ethoxylated straight chain decyl alcohol with broad/narrow distribution, Berol OX91- commercial broad range ethoxylate from a C_{9-11} straight alcohol

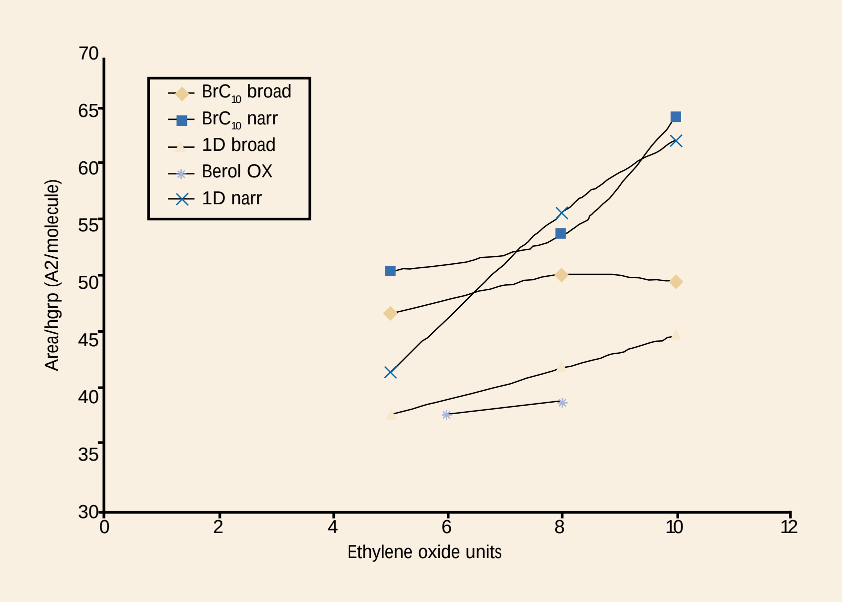

Figure 2 - Area per molecule at the air/water interface as a function of the average number of ethylene oxide units

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Overall, the branched non-ionics have higher CMCs, intuitively giving them a more hydrophilic nature.

The packing of the surfactants at the interface, as reflected in area per molecule and surface tension at CMC, was determined from the surface tension versus concentration plot where the break in the curve indicates the onset of the CMC. From the same curves the area per molecule (a_0) can be deduced[2] and the result is shown in Figure 2. The dominating feature is that larger head groups simply need more space.

Both the branching of the hydrophobe and the broadening of the EO distribution had an influence on adsorption. Surfactants with the same type of hydrophobe showed a 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 EO distribution showed similar a_0 values for bigger head groups; in other words, the packing of the hydrophilic part at the interface determines their behaviour.

Thus the influence of the hydrophobe was dominant 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 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.

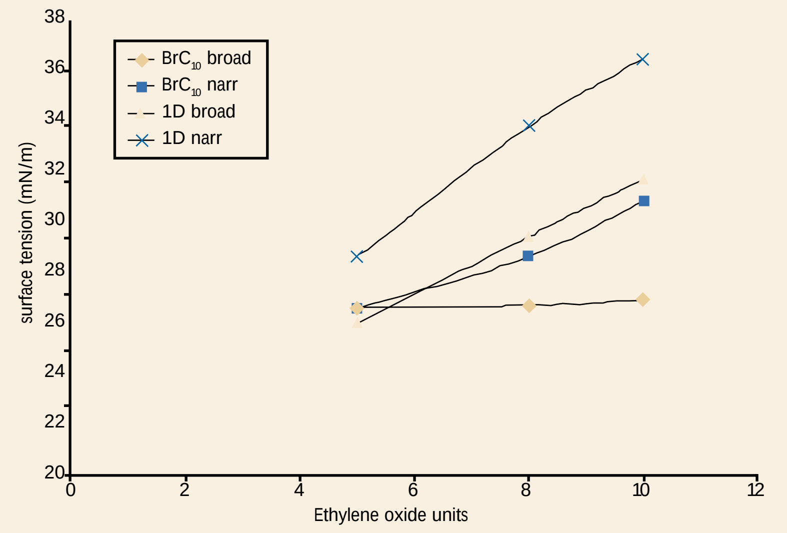

Figure 3 - Surface tension at the CMC as a function of the average number of EO units

Surface tension at or above CMC increased with increasing amounts of EO, except for the broad-range Guerbet alcohol-based compounds (Figure 3). 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. However, the special behaviour of the branched C_{10} broad-range compounds is found also in the area/molecule graph.

The most striking feature is that the Guerbet alcohol-based surfactants showed lower surface tension values, despite their relatively low adsorption compared to the straight-chain surfactants. Apparently, the branched surfactants form a more hydrophobic surfactant layer at the air/water interface. The reason for this might be found in the fact that the branch may be positioned planar to the interface, while the rest of the surfactant tails are positioned laterally to the interface. Therefore, the branch reduces the contact between water and the air, resulting in lower surface tensions for branched surfactants.

The change of the contact angle of a droplet of 0.25% surfactant solution on Parafilm as a hydrophobic model surface was followed over time with a high-speed video camera. The values after 60 seconds are shown in Figure 4, measured against amounts of EO.

Contact angles as a measure of wetting capacity are important in many practical uses for surfactants, such as cleaning hard surfaces, spreading formulations on hydrophobic surfaces like leaves and so forth. Surfactants with a higher amount of EO show higher contact angles, which is intuitively natural, since they are more hydrophilic and thus less prone to adsorb at the hydrophobic surface.

Narrow range 1-decanol-based surfactants showed a larger contact angle than similar Guerbet C_{10} alcohol-based surfactants. This observation corresponds 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 C_{10} Guerbet alcohol on Parafilm is smaller than the contact angle of neat 1-decanol. Broad range surfactants with <m> larger than six showed smaller contact angles than similar narrow-range surfactants, which again can be explained by the adsorption being tighter. Overall the branched surfactants give better wetting properties and can thus be expected to be more efficient in many applications where good wetting is essential for an optimal function.

In all, we found that the branching of the hydrophobe increases CMC and area per head group but decreases surface tension, contact angle, cloud point and foam. Here the first group of properties would indicate a more hydrophilic nature, while the second group could be described as a more hydrophobic behaviour. Thus, no straight answer to the question put forward in the title of this paper has been found.

Emulsion inversion as a tool

Another way of investigating differences between surfactants at air/water or oil/water interfaces is looking at their actual behaviour in mixtures of oil and water. This was done by mixing equal amounts of oil and water under efficient stirring in the presence of 3% of the surfactant to be investigated, thus producing an emulsion. The nature of the emulsifier decides whether the emulsion produced will be oil in water (O/W) or water in oil (O/W). Determining which is which is easy using a conductometer, since an O/W emulsion conducts electricity (is water continuous) while a W/O emulsion does not.

A complementary co-surfactant is titrated into the mixture under continued efficient stirring, using automatic equipment from Scanalys, and the conductivity is measured continuously. The emulsion will then invert when a specific amount of the co-surfactant has been added. In our case, most of the surfactants were hydrophilic and Span-80, a hydrophobic mono-sorbitane oleate, was chosen as co-surfactant.

The interesting point comes when the emulsion inverts from one type to the other. The amount of co-surfactant that has been added at that point says something about how far off you were from the start. A very hydrophilic surfactant (high HLB) would need a more hydrophobic co-surfactant in order to invert than a less hydrophilic one. Measuring and comparing the relative co-surfactant part at the inversion point gives a scale of hydrophilicity that can be compared to other characterisation measures like HLB, phase inversion temperature (PIT)[3] and surfactant affinity difference (SAD)[4].

A typical run is shown in Figure 5, where the specific conductivity is found on the y-axes and the amounts of added co-surfactant on the x-axis. The inversion points were decided according to the procedure described in Figure 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 conductivity. IP_{lower} is the amount of added surfactant in millilitres at the breakpoint of a horizon-

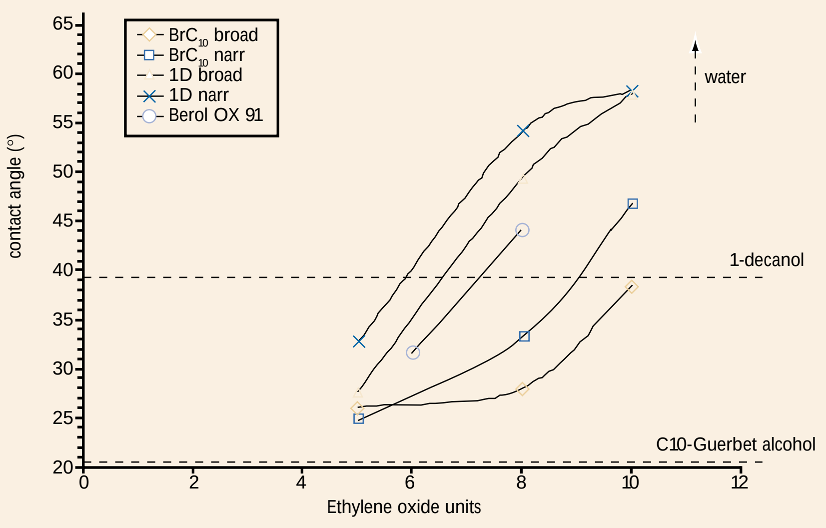

Figure 4 - Contact angle on Parafilm (60 seconds after drop formation) as a function of the average number of EO units (<m>)

Note: Temperature _ 21±1°C, 45±10%rH

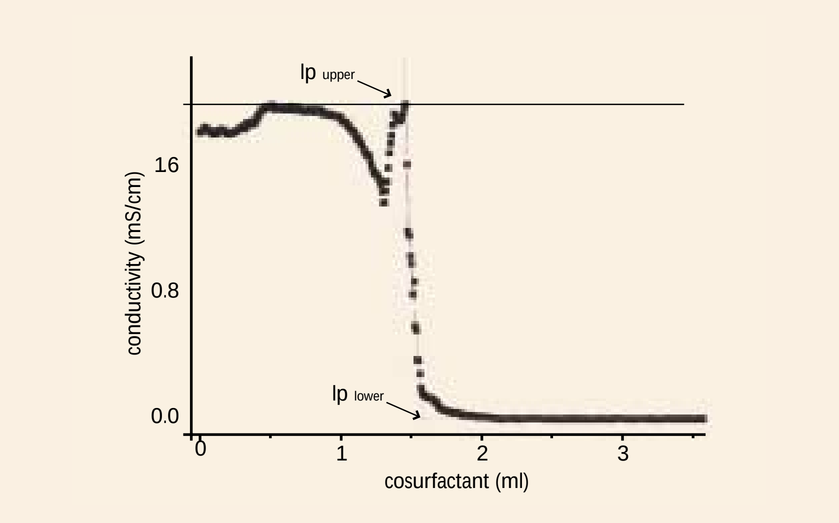

Figure 5 - Linear fits to the first and last part of the steep conductivity v. added co-surfactant for C_{10} glucoside/n-decane/water/Span 80

Note: temp = 25°C, drop rate = 0.15ml/min, stirring speed >15,000 rpm

tal line through the minimum in conductivity and a linear fit to the last portion of the steep drop in conductivity

To get a comparison with the conventional HLB system, three isomerically pure decyl ethoxylates for which the HLBs are known, $C_{10}E_8$, $C_{10}E_7$, $C_{10}E_5$, were investigated and used as references. The inversion points for the whole group of surfactants are shown in Figure 6 as a function of the degree of polymerisation (amount of EO or glucose).

Here it is clearly seen that the structure of the hydrophobe as well as the type of hydrophile and the distribution influences the hydrophilicity, changing it both upwards and downwards when compared to the reference. The most obvious effect is that of the branching, as well as the narrow distribution. Both make the product more hydrophobic.

Another interesting result is the possibility of comparing the glucose hydrophile with the EO-based one. However, it is obvious that the effect of glucose is different for the two hydrophobes. For the straight-chain C_{10}, the glucosidic part corresponds approximately to seven EOs (isomerically pure) but for the branched C_{10} it is more similar to five EOs (narrow range).

alent HLB (EHLB) from the results for the isomerically pure $C_{10}E_5$, $C_{10}E_7$ and $C_{10}E_8$ for which the HLBs can be calculated according to Griffin.The equation obtained in this manner provides a way to determine the EHLB number of any (mixture of) surfactant(s) once its inversion point in the same system (i.e. the same temperature, pressure and type of oil) is established.

Conclusions

Technical ethoxylates from Guerbet alcohols contain higher amounts of unreacted alcohol and show hydrophilic shifts like higher CMCs and larger areas per molecule at the air/water interface, but also hydrophobic shifts like lower surface tension, lower cloud points, less foam, lower contact angles against hydrophobic surfaces and lower inversion points in emulsion systems.

Technical grade $C_{10}E_{<m>}$ surfactants are blends of surfactant homologues with an average length of the EO distribution at <m>. Depending on the catalyst, the distribution of homologues can be made more or less narrow. The type of distribution influences the behaviour in different ways.

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 characterisation 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 Shinoda's PIT[3] or Salager's SAD[4]. The titration reveals the behaviour of the actual technical mixture and is thus also useful for optimising blends for specific purposes.

The answer to the question put in the title is consequently this: it depends on the environment and thus on the application! This investigation led to the development of a couple of new ethoxylated surfactants in Akzo Nobel's portfolio that were launched in 2002 and are sold under the trade names Ethylan 1005 and 1008.

These surfactants were specially adapted for cleaning purposes. The EO distribution was fine-tuned to suit this application in the best way having a low amount of unreacted alcohol and improved wetting and cleaning characteristics compared to what was found in the initial investigation described here.

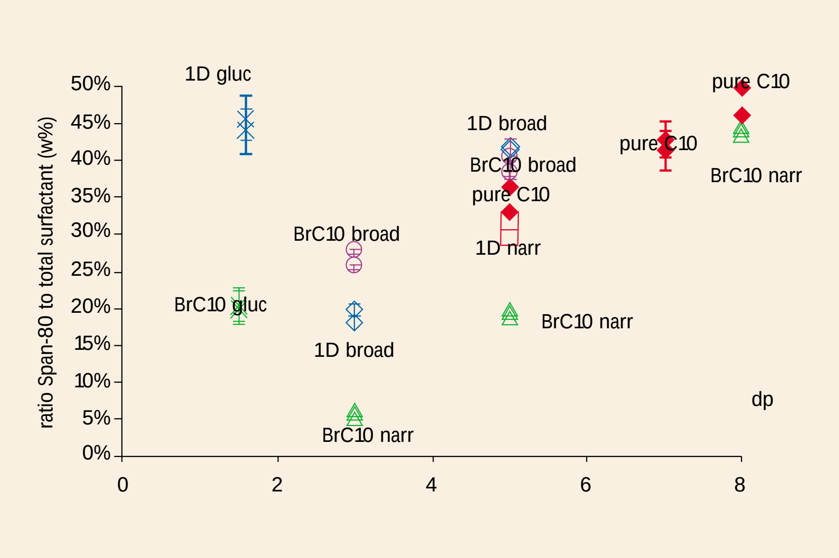

Figure 6 - Inversion points for the whole group of surfactants as a function of the degree of polymerisation (amount of EO or glucose)

References

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