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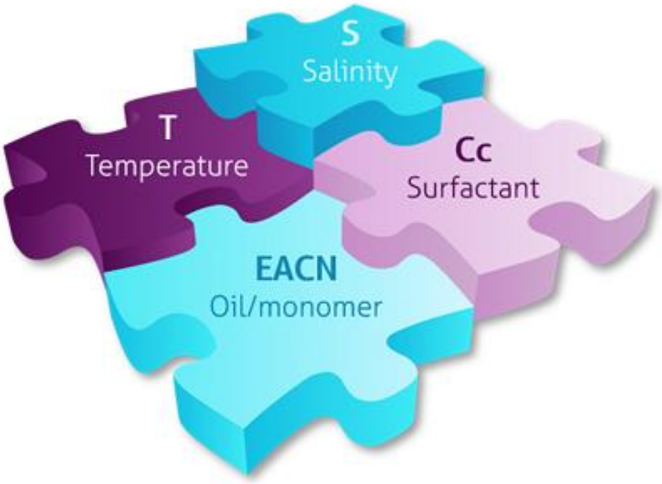
Article

Efficient Selection of Bio-Based Surfactants for Emulsion Polymerization

Sander van Loon – Mar 24, 2017

TAGS: Science-based Formulation



A proof of concept has been developed at **VLCI – Amsterdam** to showcase the process of surfactant selection via the HLD theory for emulsion polymerization. This approach, that has already been proved in the fields of personal care, household and EOR, allows a practical and fast selection of the right surfactants for the development of (micro-)emulsions.

The HLD (**Hydrophilic Lipophilic Difference**) theory is used to make profound predictions about:

1. The type of emulsion (o/w or w/o)
2. Efficiency of a surfactant in a defined emulsion system

The most effective surfactant to reach the desired type of (micro-) emulsion can be selected based upon its intrinsic parameter (Cc) and takes the following emulsion parameters into account:

- Oil
- Monomer or polymer number (EACN)
- Temperature
- Salinity, and
- Co-solvents

This article will help you understand the **practical application of HLD for emulsion polymerization**. But before that, let's see how bio-based surfactants are selected.

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Selection of Bio-based Surfactants: How is it done in the industry?

Commonly Used Methods: “Trial and Error” and HLB

The “trial and error” approach is still the most common method. In this method, varieties of surfactants are screened at different concentrations without making any prediction. This is obviously **time-consuming**. HLB values are sometimes given for surfactants, but these values are mainly applicable for EO-based surfactants, and do not give good practical guidance. Furthermore, for bio-based surfactants, the **HLB approach is usually not applicable**.

New Approach: HLD

HLD is recognized as a powerful and reliable method for effective surfactant selection and formulation of emulsions in various fields. Although little relevant literature on the subject is present, it has also been proven suitable for emulsion polymerization[1]. Although, there is currently little relevant literature on the subject is present. The ‘HLD’ is an expression of the change in chemical potential of a surfactant molecule ($\mu^{s}w - \mu^{s}o$) when it is transferred from the **oil phase** into the **aqueous phase**. HLD shifts between negative, neutral and positive values are marked by transitions between emulsions:

The general HLD equation is:

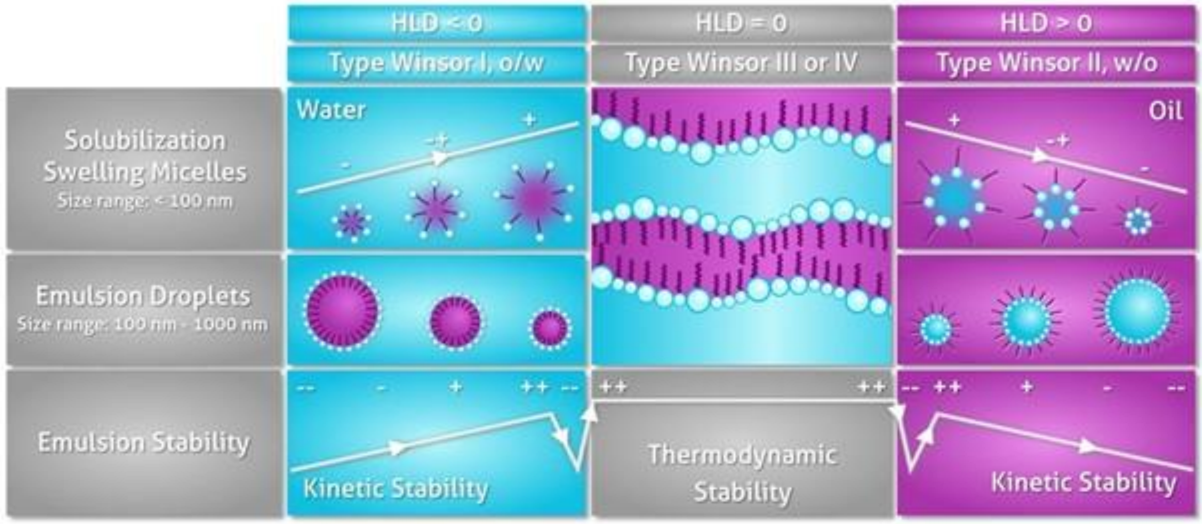
$$HLD = F(S) - k.EACN - \alpha.\Delta T + Cc + F(A)$$

- **F(S)** is a function of salinity: as S increases, so does HLD. For non-ionics **$F(S) = b*S$**, and for ionics **$F(S) = \ln(S)$**.
- **EACN** is the number of **carbon atoms** in the **linear alkane** with equivalent behavior to the oil. As EACN and **lipophilicity increase, HLD decreases**.
- The value of the **coefficient k** depends on the type of surfactant used, with the standard value being **$k=0.17$**.
- The effect of the temperature difference with the reference value of 25°C is characterized by the **coefficient α**. Its value is dependent on the type of surfactant used, such as:

    - **+0.01** for ionics
    - **-0.06** for ethoxylates
    - **0** for APGs, etc...

- The **Cc** value is the characteristic **curvature of the surfactant**.
- Finally, **F(A)** is a contribution of a **co-surfactant** or alcohol, that may depend on its nature and concentration.

When **HLD = 0**, the **thermodynamically stable** state is reached, and all parameters are **balanced**. This results in a micro-emulsion. From there, slightly negative or positive values of HLD give respectively types I (o/w) or types II (w/o), emulsions that are typically formulated.



The beauty of this approach relies on its **versatility**. All kinds of oils, monomers and polymers can be **characterized with an EACN**, as well as **surfactants with Cc values**. This allows for accurate ingredient matching, resulting in more stable emulsions.

Once the EACN value of an oil is known, the required Cc value is calculated from the equation to formulate the required emulsion. It is also applicable to blends; the resulting EACN or Cc being the sum of each EACN or Cc multiplied by their respective molar fraction.

Databases of EACN and Cc values already exist in order **to properly select suitable surfactants**[2,3], but they are still very limited. There is therefore a need to extend this to more oils and surfactants. It would be great if the suppliers provide these parameters as well.

Why is HLD effective for emulsion polymerization?

By ensuring that the HLD is slightly lower than 0 (type I, o/w), the maximum amount of surfactant molecules are present at the **monomer droplets interface**. That too, with the minimum added surfactant. Therefore, the surfactant is used at its utmost efficiency. The required Cc is calculated by implementing the following variables in the HLD equation:

- Composition of the monomer phase
- Salinity
- Presence of co-solvent, and
- Temperature profile of the reaction

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The emulsion stability is a major concern when performing emulsion polymerizations. Oil separation, coalescence of the droplets and Ostwald ripening all affect the final product by creating:

- Agglomerates
- Monomer residues, or
- Undesired polymerization grade

When the surfactant (or blend of surfactants) is selected to reach the required Cc value, the emulsion is stable and can be prepared with the lowest energy input. Therefore, it's very **effective approach for emulsion polymerization**!

High Throughput Preparations

The co-polymerization of a well-known system of **Butyl Acrylate (BA)** and **Vinyl Acetate (VA)** (**30:70**) is chosen to illustrate the surfactant selection via HLD for emulsion polymerization. HLD scans are performed in accordance with the **theory to characterize both monomers and surfactants**, rationalizing the surfactant selection.

In order to speed up the HLD characterization of these compounds, **the High Throughput FORMAX is used**. This automatically prepares a large number of samples, in parallel and on small scale. Likewise, the emulsion polymerization reactions are carried out with the FORMAX HT platform in an **automated and parallel way**.

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HLD Scans for the Determination of EACN and Cc Parameters

The scans are performed on both monomers and surfactants. They are used as the **only unknown species** in an oil/water/surfactant system whose HLD parameters are known. Several samples of such a system are prepared by **modifying only one of the parameters** of the HLD equation (typically the salinity or the temperature) in a controlled way. This is done in order to cover the different emulsions types (I, II and III).

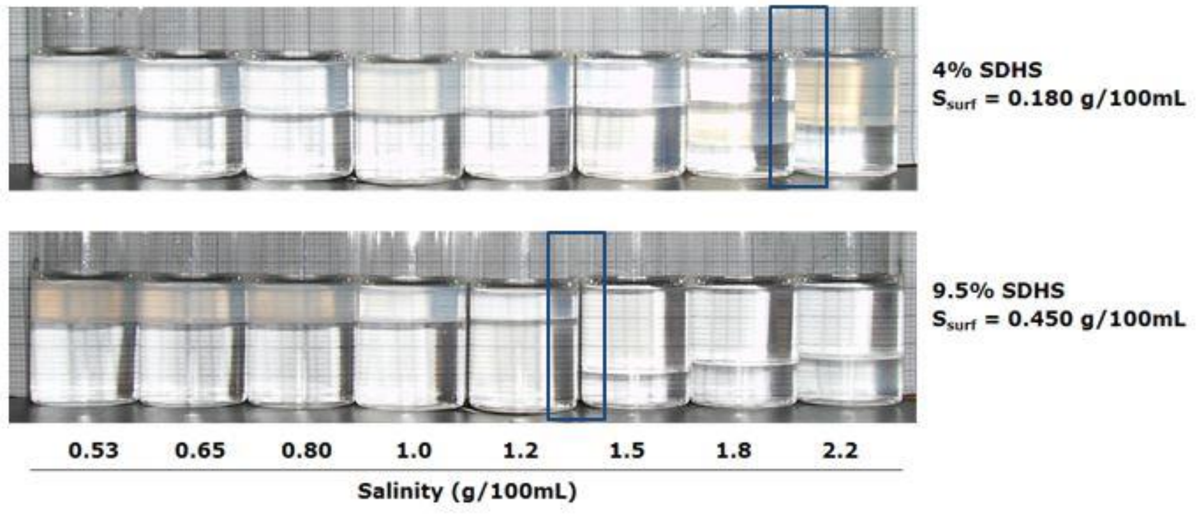
o/w (Type I, HLD < 0) → w/o (Type II, HLD > 0), via **Type III (HLD ≈ 0)** gives the point where **HLD = 0**

The HLD parameter of the unknown species can then be calculated by filling all the other parameters in the HLD equation. The samples are deliberately prepared in such a way that phase separation is obtained **quickly**, in order to easily visualize the different emulsion types.

Calculating EACN of Monomer Blends

Here, the 2 monomers are characterized separately. Once the EACN values are obtained for these 2 building blocks, the EACN of any monomer blend can be calculated. The scans are made with a surfactant whose **Cc is known in a 50:50 (vol) blend** of salted water and monomer, the only unknown component.

The picture below displays the scans for EACN's determination of butyl acrylate (BA), with the phase transitions highlighted:



Determining EACN of butyl acrylate

These scans lead to **$EACN_{BA}$ = -1.9±0.2**

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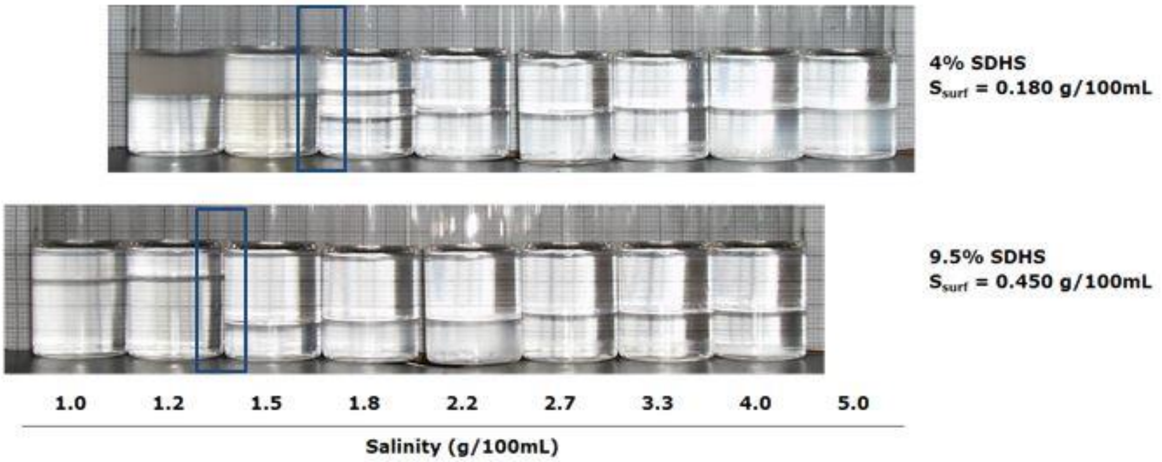
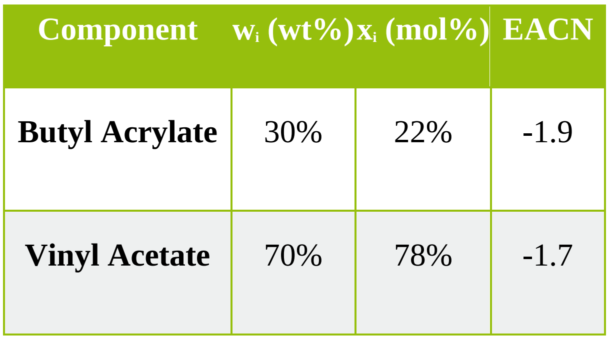
The picture below displays the scans for EACN’s determination of vinyl acetate (VA), with the phase transitions highlighted:



Determining EACN of vinyl acetate

These scans lead to **EACN_{VA} = -1.7±0.3**

In this case, the polymerization is based on **30:70 - BA:VA** blend. The calculation for the EACN of the monomer blend is given below:



Component	w_i (wt%)	x_i (mol%)	EACN
Butyl Acrylate	30%	22%	-1.9
Vinyl Acetate	70%	78%	-1.7

Calculation for the EACN of the monomer blend

Knowing that **EACN = Σx_i . EACN_i**, this leads to **$\text{EACN}_{\text{blend}}$ = -1.7**

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Applying the HLD Equation for Surfactant Selection

The HLD value to emulsify the 30:70 BA:VA blend should be slightly lower than 0, because it:

- Ensures a very **stable type I** (o/w) pre-emulsion (monomers and surfactants emulsified in an aqueous phase)
- Offers a **narrower particle size** distribution, and
- **Lowers emulsification** energy requirement

$$HLD = F(S) - k.EACN - \alpha.\Delta T + Cc$$

Knowing that the polymerization reaction is performed at zero salinity, the HLD equation indicates that the surfactant should have a Cc close to -0.6 (for a 50:50 (vol) blend of monomers:water, at 25°C). Then the **modelling tool**[4] gives an estimated Cc value close to **-0.2** for a **65:35 - monomers:water** pre-emulsion blend.

Lauryl Glucoside is selected from VLCI database as it exhibits the following advantages:

- It has **Cc ≈ -0.2** which is, within the required range of Cc values
- It is **Bio-based**
- Also, it is **APG surfactant**. That is, the parameter **α=0**, meaning that the temperature has no influence on the type of emulsion. This is a great advantage as the reaction takes place at 75°C while the pre-emulsion is being prepared at room temperature

Emulsion Polymerization & Performance of HLD Predicted Surfactant

The performance of lauryl glucoside (LG) is evaluated against sodium nonylphenol ether sulfate 10 EO (NPES). It is a known surfactant for emulsion polymerization. The experiment was performed at different concentrations, with **oleyl cetyl ethoxylate 25 EO (OC25)** used as a **co-surfactant**.

Pre-Emulsions Stability

This time-lapse video shows the **stability test** over 1 hour for the different samples.

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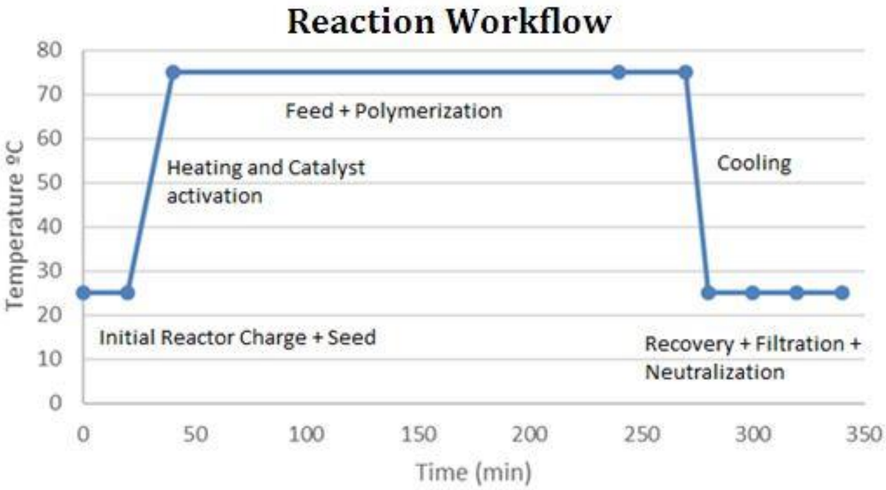
Samples on Left-Hand Side:	**Samples on Right-Hand Side:**
NPES - 2%	LG - 2%
NPES - 1%	LG - 1%
NPES - 0.5%	LG - 0.5%
NPES - 0.25%	LG - 0.25%

Reaction Process

The reaction is performed by **continuous addition of the pre-emulsion** into the **initial reactor charge**, which contains the initiator (**potassium persulfate**). The reaction steps and temperature profile are displayed on the diagram below:



Emulsion Polymerization Process

The resulting polymer dispersions are evaluated according to the following criteria:

- Presence of **agglomerates or sediment** in the polymer dispersion

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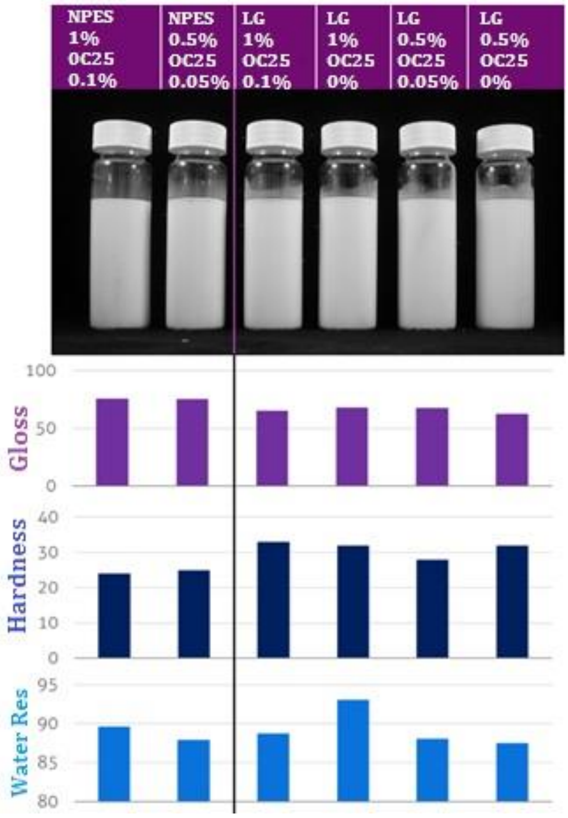
- Solid or gelled **residues** in the reactors
- **Dry film properties**, such as:
    - Gloss
    - Hardness
    - Water resistance (150 microns wet film thickness)

These simple evaluations can validate the surfactant selection before committing to deeper analytical determinations, like:

- Particle size distribution
- Molecular weight, and
- Grade of ramification

Results

None of the reactions produces significant residues in the reactors. Also, none of the produced dispersions contain **agglomerates or sediments**. The picture below displays the different emulsions together with their respective film properties.



Different Emulsions with Their Respective Film Forming Properties

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The replacement of **NPES by lauryl glucoside** in the emulsion polymerization of 30:70 - BA:VA leads to stable polymer dispersions. Also, the corresponding films give **higher hardness and better water resistance**, while reducing the need for a co-surfactant.

Conclusion

Monomers can be characterized as well as novel and complex surfactants. This allows **green chemical specialties** to be selected in a more **predictive fashion**. This R&D strategy saves time and money by:

- Improving the stability, and
- Reducing surfactant usage and energy input

Through this example, it was shown that the HLD approach can be **practically and efficiently applied** to surfactant selection for **emulsion polymerization**. Therefore, extension of existing databases with HLD parameters would support the work of formulators to select **surfactants for emulsions**. Also, polymer dispersions and should be seriously considered as an addition or an alternative to conventional development approaches.