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Article

Predictive Cosmetic Formulation via HLD-NAC: From Triphasic Emulsions to Single-phase Emulsions

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TAGS: Surfactants/Cleansing Agents

While selecting surfactants in the cosmetic industry, the most commonly used methods include:

1. **The "trial and error" approach**, which is still the most frequent method. A variety of surfactants are screened, at different concentrations, without using any predictions. This is obviously time-consuming.

2. **HLB values** - which 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.

Fortunately, we now have a new approach: HLD-NAC (Hydrophilic Lipophilic Difference - Net Average Curvature). It a powerful and reliable method for effective surfactant selection and formulation of emulsions in various fields including cosmetics and personal care industry.

The beauty of this approach relies on its versatility: all kinds of oils can be characterized by EACN values, as can surfactants by their Cc values. This allows for accurate ingredient matching, resulting in more stable emulsions with lower amounts of surfactants and energy input to produce them.

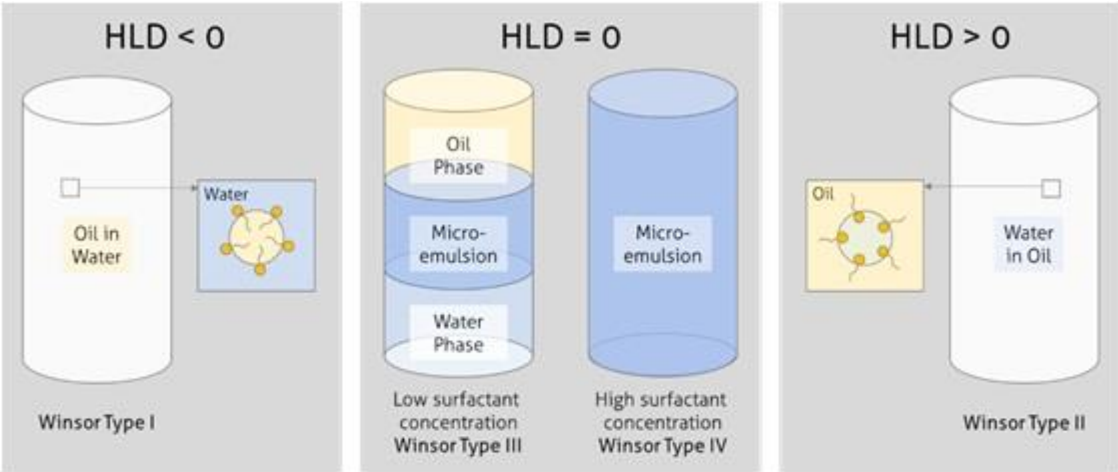
Let's understand how this theory can help in formulating triphasic & single-phase emulsions...

Applying HLD-NAC for Triphasic and Single-phase Emulsion Formulations

The formulation of regular triphasic formulations is usually done by combining liquids of different densities that are immiscible. However, this method often involves the use of organosilicon or fluorinated liquids which are not always desired in cosmetic and personal care products.

The HLD-NAC can be used to characterize (bio-based) surfactants and oils which then can be used to formulate, among others, the type III emulsions. Indeed, Type III emulsions are triphasic systems that are formed at HLD = 0 at low surfactant concentration. Furthermore, at HLD = 0, an ultralow interfacial tension is reached, therefore a *triphasic emulsion will be able to boost* *cleaning performance* (not only appearance). Adding a higher amount of surfactant(s), the middle phase can be increased up to a single-phase system.

Once the EACN of the oil (or oil blend) to be used in the tri-phase formulation is determined, it is possible to select a **(blend of) surfactant(s)** with the appropriate Cc value to reach HLD=0 and obtain a type III emulsion, i.e. tri-phase product. From that point, all other types of emulsions can be formulated, as seen below:



Applying HLD-NAC for the Formulation of Triphasic and Single-phase Emulsions

Practical Example: From 3-phase to Single Phase Emulsion

Our project consisted of the development of a micro-emulsion-based makeup remover in which HLD is 0. Type III and Type IV micro-emulsions have been formulated to obtain high cleaning performance. Furthermore, a type III system (triphasic) offers an attractive appearance to the formulated product.

Characterization of ingredients allows the formulation of Type III/IV micro-emulsions. The table below shows the used ingredients and their related HLD parameters.

Product	INCI	HLD behavior
PUROLAN® IHD	Isohexadecane	EACN =12
PUROLAN® IDD	Isododecane	EACN =10
PUROLAN® PD-LO	Pentylene Glycol	Negative contribution
PUROLAN® OD-C	Caprylyl Glycol	Positive contribution
AOT	Diethylhexyl Sodium Sulfosuccinate	Cc = 2.55

First, **AOT (Diethylhexyl Sodium Sulfosuccinate from Sigma Aldrich)**, a mild surfactant highly suitable for body washes/cleansing formulations, was used as the main surfactant. The well-known HLD behavior of AOT (Cc= 2.55) made it suitable for isoparaffins EACN characterization (Isohexadecane and Isododecane provided by **LANXESS**).

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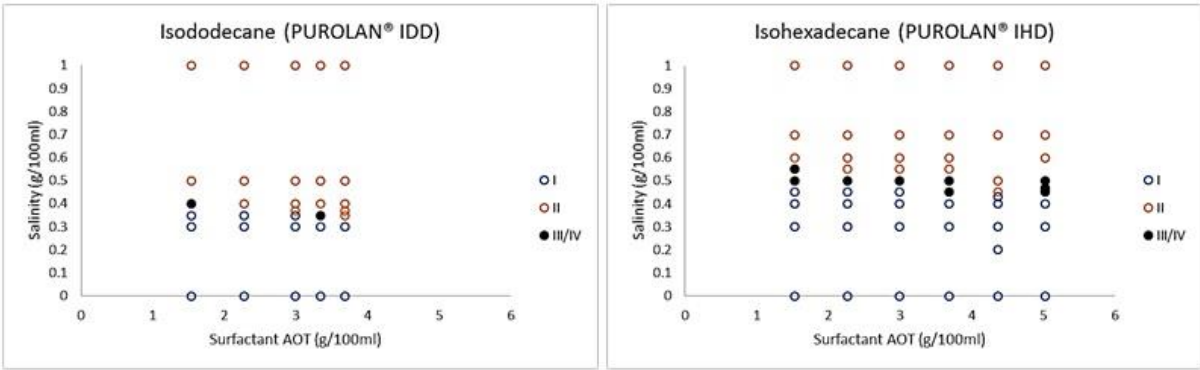
The figures below show the phase transitions studies of salt scans at different surfactant concentrations.



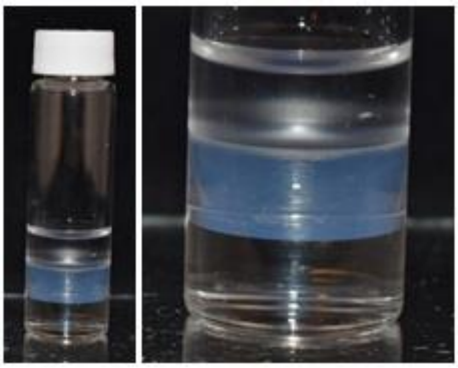
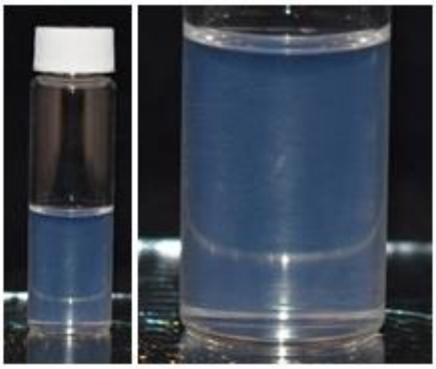
Phase Transitions Studies of Salt Scans at Different Surfactant Concentrations

Once the type III and IV micro-emulsions were defined, pentylene glycol and caprylyl glycol (from LANXESS) were used to:

- Bring transparency
- Adjust the separation time (in case of type III), and
- Give antimicrobial protection

After manual shaking; the type III micro-emulsion separates back into the three distinct phases within a couple of minutes. Type IV was developed to show that once HLD=0 has been reached, it is possible to develop the single-phase micro-emulsion by adding more of the surfactant(s).

Furthermore, HLD can guide the preparation of Type I or II standard emulsions. Since, at HLD=0 the surface energy is minimized, reducing the energy input to prepare the emulsions with smaller particles and at reduced surfactant usage is possible.

Type III Micro-emulsion	Type IV Micro-emulsion
	
INCI • Water • Isohexadecane • Isododecane	**INCI** • Water • Isohexadecane • Isododecane

• Diethylhexyl Sodium Sulfosuccinate • Pentylene Glycol • Sodium chloride • Caprylyl Glycol	• Diethylhexyl Sodium Sulfosuccinate • Pentylene Glycol • Sodium chloride • Caprylyl Glycol

Conclusion

As seen in the practical example of a triphasic cleaner, HLD-NAC is a beautiful and versatile method, providing predictive formulation parameters. This is one example among many others, as the method is applicable to all types of emulsion systems and offers a controlled approach for their fine-tuning.

When the HLD = 0 point has been obtained, it is then possible to **select the best surfactant** (blend) at the lowest concentration to develop the (micro-)emulsion with the lowest energy input. Adding perfumes or alcohols into emulsions can make them collapse, but HLD-NAC can quantify the influence of these additives too and give specific guidance on how to rebalance the system to obtain a stable (micro-)emulsion.

About the Co-Author

Alejandro Gutierrez is the Innovation Manager of VLCI (Van Loon Chemical Innovations), an independent laboratory providing innovative and practical R&D services within the formulation industry. With the unique approach by combining applied formulation science with High Throughput (HT) screening, VLCI aims to move the formulation industry to a higher level, creating flexibility, predictability, new insights/products and efficiency.

He holds a MSc in Chemistry and Postgraduate studies in Innovation Management and New Product/Service Development. He has become a multidisciplinary expert after 10 years of technical experience in formulation science, part of the VLCI team since 2011. Nowadays he is located at VLCI-BCN facility and in charge of VLCI Technology Distribution Centre, helping to connect companies to the most promising formulation technologies and solutions.

The authors would like to acknowledge Ana Hijano for her contribution to this article