Article

Efficient Approach for Bio-Based Replacement of Monomers

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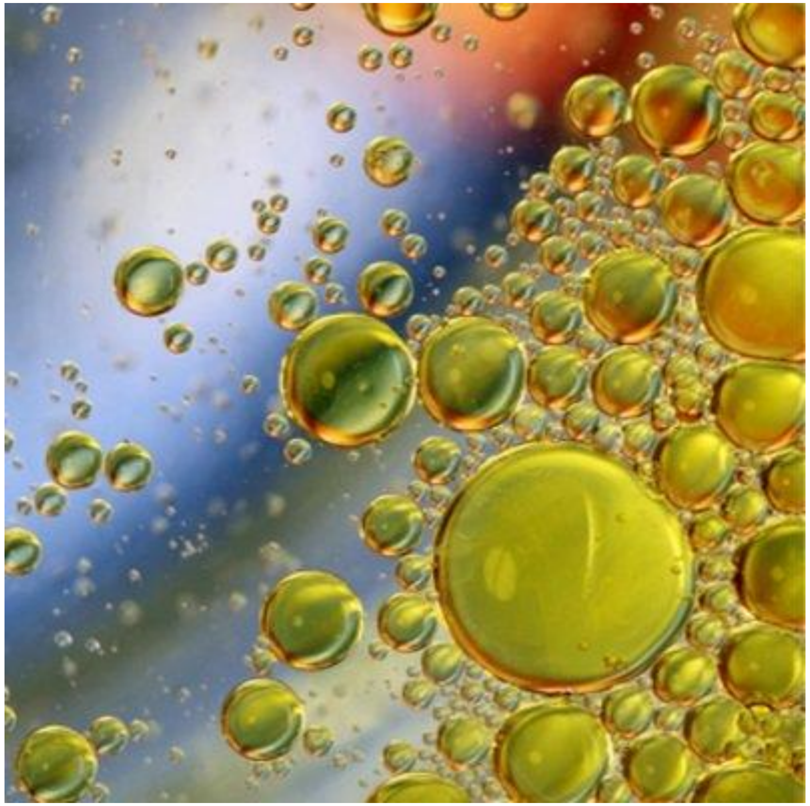
In emulsion polymerization, the replacement of standard monomers with bio-based monomers requires a firm understanding of the total system, if it is to be formulated properly. The HLD-NAC approach can be used to characterize the constituents in a polymer emulsion so that, more rational adjustments can be made to the surfactant system, while maintaining stability and performance.



The **Hydrophilic Lipophilic Difference - Net Average Curvature**(HLD-NAC) theory in a defined emulsion system, is used to make profound predictions about:

- Type of emulsion (o/w, w/o), and
- Efficiency of surfactant

HLD-NAC allows for the selection of the **optimal surfactant** to obtain the desired type of (micro-) emulsion by taking the following parameters into account:

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

The previous article on efficient selection of bio-based surfactants, described a practical application of HLD-NAC for emulsion polymerization. There, a bio-based surfactant was selected to emulsify a blend of monomers. This article sets out to demonstrate the use of HLD-NAC in replacement of the **water-soluble co-monomers** used in an emulsion polymerization.

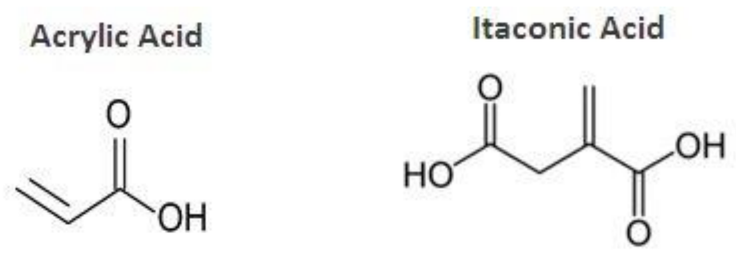
Let's begin by understanding the effect of replacing acrylic acid with itaconic acid in a well-known emulsion polymerization system.

Replacing Acrylic Acid with Itaconic Acid

VLCI participated in the **BioQED project** (www.bio-qed.eu), a European project for developing **bio-chemicals** from renewable sources. Its main goal is to open new industrial routes for the production of important chemicals from renewable sources rather than traditional petrochemical sources.

In this framework, an entrepreneurial consortium was built. It's joint ambition was to generate hard evidence and collect all the technical and economic key design parameters needed for investment decisions for the first industrial production plants of the bio-based building blocks: **1,4 butanediol (BDO)** and **itaconic acid (IA)**. The consortium is based on strong industrial leadership on both of the selected products and covers the full supply chains for bio-based BDO and IA.

In this example, itaconic acid (IA) is used to replace acrylic acid (AA) in the **copolymerization reaction** of Butyl Acrylate (BA) and Vinyl Acetate (VA) (30:70). It is a well-known system for emulsion polymerization.



High Throughput Preparations

HLD scans are performed in accordance with the theory to assess the HLD behavior of AA and IA. Also, the scans are executed, if adjustments on the HLD balance need to be made to preserve the equilibrium of the system after the IA replacement.

High Throughput Preparations

Determination of the Co-monomer Effect on HLD Equation

Approach

The co-surfactant / co-solvent / alcohol component of the HLD equation, F (A), is a linear function of the concentration of co-surfactant:

$$F (A) = \gamma . [co\text{-}surfactant]$$

For co-surfactants, one might consider that the **Cc** of the emulsion is affected, being more like an "**effective Cc**" with $\mathbf{Cc_{eff} = Cc + f (A)}$. In order to determine effect on the HLD equation of such an ingredient, two contribution scans must be performed.

In a contribution scan, the unknown co-surfactant is used to replace a certain percentage of surfactant or oil of a known regular scan. The contribution of the unknown ingredient can be assessed by knowing the Cc of the replaced surfactant and the other parameters of the scan. By preparing several scans with different replacement percentages, it is possible to determine the **γ coefficient** of the unknown ingredient.

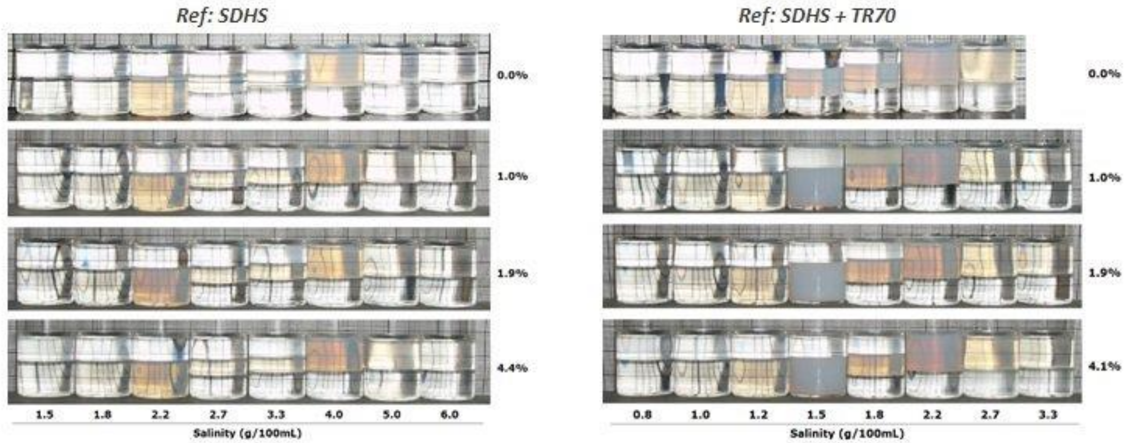
Two contribution scans are performed in order to assess both the surfactant and co-surfactant nature of the species. Indeed, depending on its concentration the same ingredient may act more as a **co-surfactant ($Cc_{eff} = Cc + f(A)$)** or as a **pure surfactant ($Cc_{eff} = \Sigma x_i . Cc_i$)**. A similar approach exists for oils and co-solvents.

Results

This study focuses on the **replacement of acrylic acid (AA) by itaconic acid (IA)** in the copolymerization reaction of Butyl Acrylate (BA) and Vinyl Acetate (VA) (30:70). Both their HLD contributions are studied via two contribution scans. The two reference scans used are:

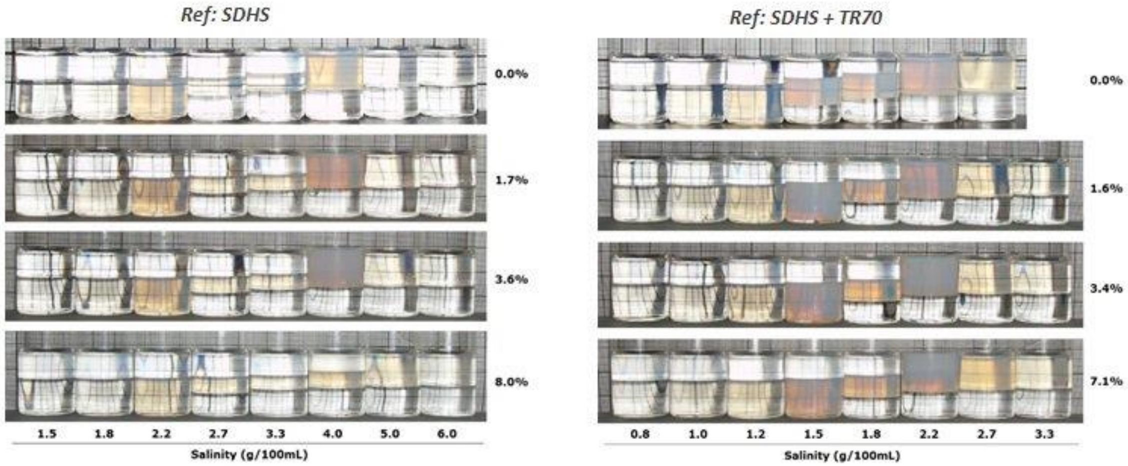
1. Salt scan with 4wt% of Sodium Dihexyl Sulfosuccinate (SDHS) and Toluene
2. Salt scan with 4wt% of a blend of SDHS and Aerosol TR70 (Sodium Bistridecyl Sulfosuccinate) and Toluene

The first set of pictures displays the contribution scans for acrylic acid at different surfactant replacement percentages (wt %) with the phase transition highlighted.



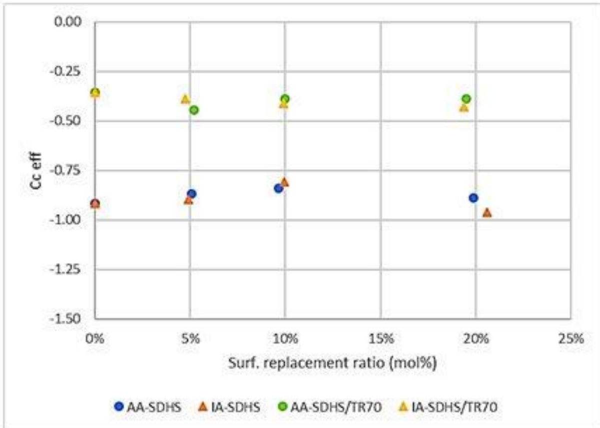
Contribution Scans for AA at Different Surfactant Replacement Percentages

The second set of pictures displays the contribution scans for itaconic acid at different replacement percentages with the phase transition highlighted.



Contribution Scans for IA at Different Surfactant Replacement Percentages

The graph below shows the **evolution of Cc_{eff} of the 2 surfactant systems** with the replacement ratio (mol %) of AA or IA.



Evolution of CC_{eff} of Surfactant Systems with the Replacement Ratio

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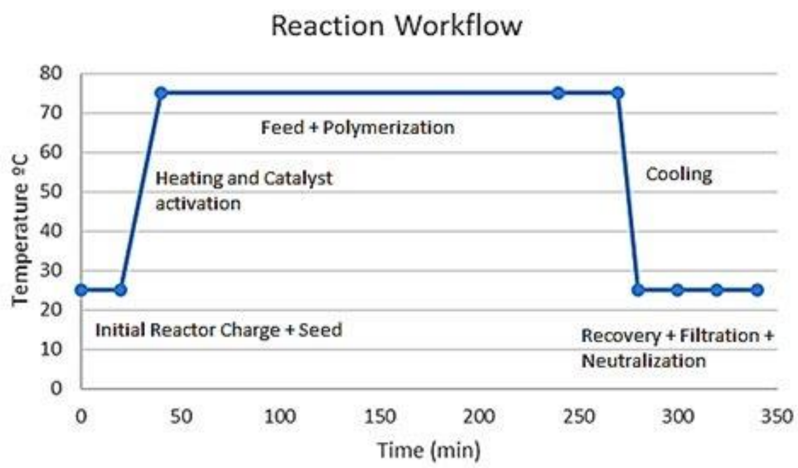
This shows that neither AA nor IA has an influence on the HLD equilibrium of the system. Therefore, IA can be used to replace AA without disturbing the emulsion. As a result, the monomer blend requires the same Cc and the same surfactant system can be used for the emulsion polymerization, working with either AA or IA.

Synthesis via HT

In the previous article, **lauryl glucoside** (LG) was selected using HLD-NAC data implementation to successfully replace sodium nonylphenol ether sulfate 10 EO (NPES) in the emulsion polymerization of Butyl Acrylate (BA) and Vinyl Acetate (VA) (30:70). The effect of the substitution of AA by IA is studied in several reactions using either surfactant. Oleyl cetyl ethoxylate 25 EO (OC25) is used as a co-surfactant with NPES but not with LG. This is because, this co-surfactant lowers the film properties when used with LG as shown in the previous article.

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

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

- Presence of agglomerates or sediment in the polymer dispersion
- Solid or gelled residues in the reactors
- Dry film properties: 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

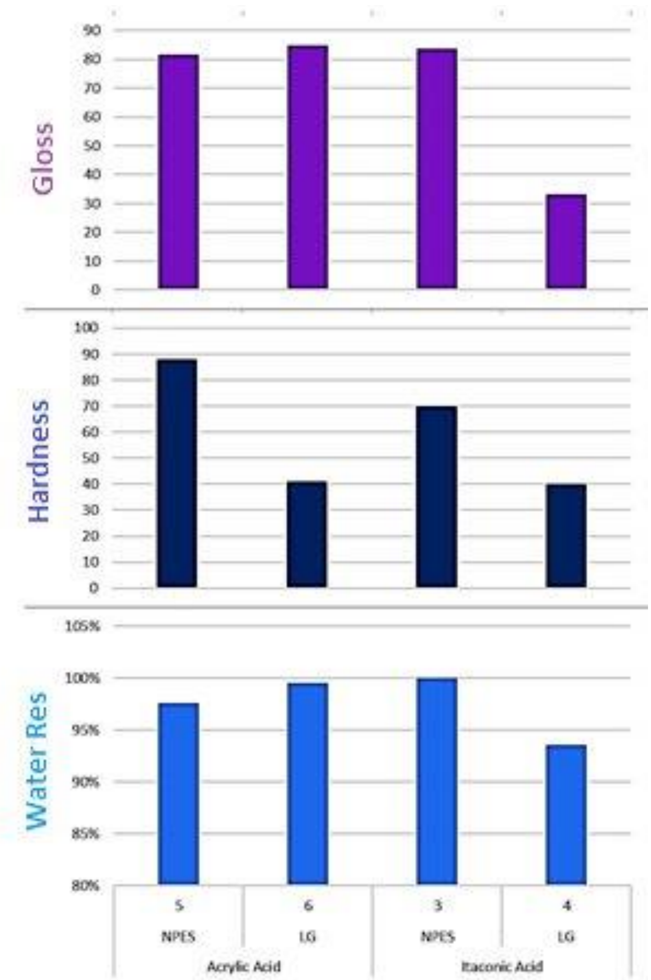
None of the reactions produces significant residues in the reactors. Apart from the dispersion with **NPES and IA** that shows a little sediment, none of the produced dispersions contain agglomerates or sediments.

The picture and the graphs below display the different emulsions together with their respective film properties.

Different Emulsions and their Respective Film Properties

Surfactant	NPES 1%	LG 1%	NPES 1%	LG 1%
Co-surfactant	OC25 0.1%	-	OC25 0.1%	-
Co-monomer	Acrylic Acid 0.5%		Itaconic Acid 0.5%	

Different Emulsions and their Respective Film Properties



Film Forming Properties of Emulsions

It could be observed that the sample with LG and IA gives a lower gloss, hardness and a slightly lower water resistance. The sample with LG and AA also gives a lower hardness. This might be due to the concentration of surfactant that is too high.

Indeed, **lauryl glucoside - The surfactant selected via HLD-NAC, is more efficient than NPES**. Therefore, lower quantities are needed. Further, development of the emulsion should be carried out in order to study the influence of the **reduction of LG concentration** on the properties. Preliminary experimental work has already been performed in that sense and gave very promising results.

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Conclusion

It is shown that the HLD-NAC approach can be applied to make rational decisions for the replacement of a conventional monomer by a bio-based monomer. In this example, neither AA nor IA contributes to the HLD balance. This means that, **no correction of the Cc is required** and that the selection of surfactants and their ratios are as predicted.

Indeed, the replacement of AA by IA does not cause any problems during the emulsion polymerization and nor does it give stability issues. Using the traditional surfactant system only a slight reduction in hardness of the film with IA is observed, compared to the AA-based polymer.

In addition, by using the bio-based surfactant: The gloss of the IA-based polymer film is then significantly reduced, and the water resistance is only slightly decreased. As this bio-based surfactant is more efficient, lower concentrations are being screened and already show increased gloss values.

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