Base oil and emulsifier selection principles - a metalworking fluid emulsion stability study

Metalworking Fluids

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INTRODUCTION

There is an intimate relationship between the formulation and the performance of metalworking fluids. To investigate how the formulation parameters and water hardness affect the emulsion stability, a series of emulsions have been formulated where the base oil, the emulsifier selection and water hardness were parameters changed independently, in order to investigate how these parameters, affect properties like the droplet size distribution and emulsion stability.
Results were obtained and analysed for naphthenic, Group I and Group II base oils. The conclusions of this study will hopefully find use as a component selection guide to metalworking fluid formulator across geographical regions, with varying water hardness, and different access to base oils suitable for metalworking emulsion formulations.

EMULSION STABILITY

Emulsion stability is key to metalworking fluid (MWF) usefulness. Investigations of the relationship between formulation and emulsion stability this is a first step towards better understanding of the complex chemistry of a fully formulated MWF.

Test parameter in this study were base oil type selection, water hardness and emulsifier selection.
We sought to understand how the properties of the base oils, especially solvency, and the water hardness (°dH) would influence emulsion stability over test period up to one week.
Emulsifier (surfactant) type and Hydrophile-Lipophile Balance (HLB) would also be important variables.

EXPERIMENTAL WORK

Four ISO VG 22 (~100 SUS) Base oils investigated

- Naphthenic T 22, Aniline Point (AP) = 76 °C
- SN 100 (AP = 100 °C)
- New Range 100 (AP = 101 °C)
- HP 4, a Group II base oil (AP = 108 °C)
- Water hardness
  - De-ionised, °dH = 0 (similar to Reverse Osmosis)
  - Synthetic hard water, °dH = 20 (357 ppm $CaCO_3$, e.g. Los Angeles area)

- Emulsifiers (Surfactants)
  - **Span 80** (Sorbitan monooleate), HLB 4.3, Lipophilic
  - **Tween 80** (Polyethylene glycol sorbitan monooleate), HLB 15, Hydrophilic
- One commercially available emulsifier additive package
  - A newly developed range of non-ionic emulsifiers from Solvay
- Solubiliser (co-emulsifier, coupling agent)
  - Butyldiglycol

Emulsions were formed, based on the four base oils

- Naphthenic, two Group I, Group II
- Span 80/Tween 80 blends
  - HLB range from 9 to13
- The commercial emulsifier package at a recommended HLB
- Water hardness, soft or hard
  - Soft water (°dH 0)
  - Synthetic hard water (°dH 20)
- Conditions for emulsion formation
  - Mild agitation for 3 minutes

- We utilized two complementary approaches
- **1. Droplet Size Distribution (DSD)**
  - Determined at high dilution
  - Distribution changes over time
  - Coalescences can be detected
- **2. Light transmission and back scattering**
  - Determined "as-is" on the real liquid systems
- Emulsion stability is correlated to the growth of droplet size by coalescence
- Emulsion stability can be directly assessed by light scattering and vertical scanning
  - Sedimentation, creaming, layering etc. can be observed directly and plotted time-resolved

Emulsion phase destabilisation kinetics determination

- Emulsions were formed, based on the four base oils
  - Naphthenic T 22, SN 100, New Range 100 & HP 4 Group II
- Span 80/Tween 80 blends
  - HLB range from 9 to13
- Water hardness, soft or hard
  - Soft water (°dH 0)
  - Synthetic hard water (°dH 20)
- Conditions for emulsion formation
  - Mild agitation for 3 minutes
- 18 samples per base oil

In Figure 1 below, the bars show the optimum HLB value in the Tween/Span system for a naphthenic base oil. An emulsion droplet size of 1 µm or less gives a hardly visible set of bars at HLP 11.5 and 12. The purple line shows the TSI emulsion stability index value, where again a low number, meaning the lowest rate of change, shows the best experimental conditions.

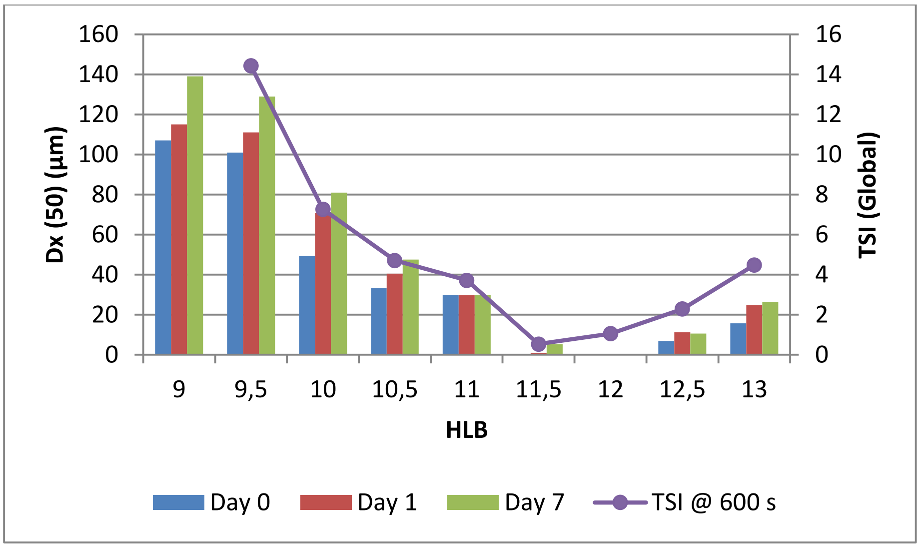


Figure 1. Droplet Size Distribution (DSD) and Turbiscan Stability Index (TSI) emulsion stability for a naphthenic base oil in the Tween/Span emulsifier model system.

RESULTS AND DISCUSSION

- The trend of destabilisation kinetics by TSI can be observed over the four-day measurement period
- The longer observation and measurement time clearly discriminate the test fluids emulsion stability properties
- The correlation b/w DSD and TSI is ***best*** for the very stable emulsions, e.g. naphthenic base oil systems
- The commercial emulsifier package delivers stable emulsions over days and weeks
- Three bands of behaviour are observable for these systems
- Stability order Naphthenic > SN 100/NB100 (Group I > HP 4 (Group II)

CONCLUSIONS

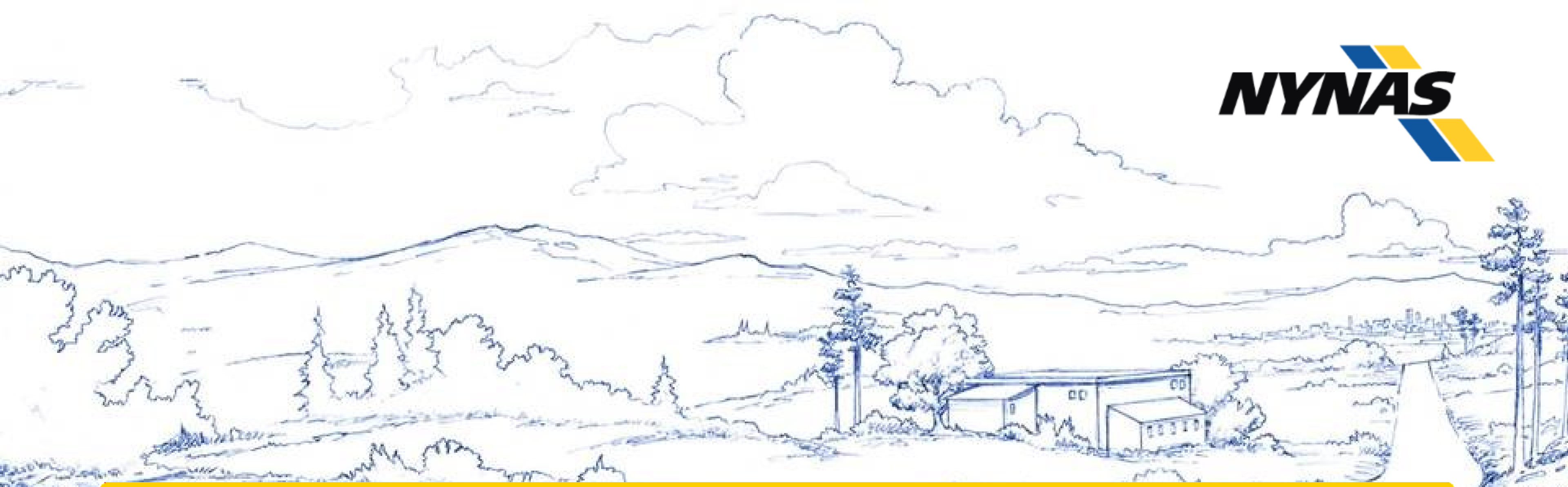
- Emulsion stability is a key requirement of emulsion-type metalworking fluids
- Emulsion stability can me modelled in test systems
- The emulsion thickness method intuitively is closer to the real and observable emulsion fluid systems
- The droplet size distribution (DSD) method offers a wealth of data, and can generate a well-resolved mapping of the stability properties
- The two methods, DSD and TSI, correlate quite well in practice
- In both these models, a merit of performance rating may be observed for the base oils and emulsifiers studied
- The Naphthenic base oil emulsions display the highest stability, followed by the Group I and Group I replacement base oils
- The solvency, as indicated by the aniline point, mirror this order, and thus might play an important role for emulsion stability in the systems investigated

ACKNOWLEDGEMENTS

A loan of a Turbiscan LAB instrument loan provided by Gammadata, Sweden, and samples of a newly developed range of non-ionic emulsifiers from Solvay, France, as well as kind assistance in formulation guidelines and discussions is gratefully acknowledged.

KEYWORDS

Base oil selection: Emulsifiers: Water hardness: HLB: Emulsion stability



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The 71st STLE Annual Meeting, Las Vegas, May 2016

Prof. Dr. Thomas Norrby

Dr. Pär Wedin

Nynas AB, Sweden

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LAS VEGAS
May 15-19, 2016

Nynas was founded in 1928

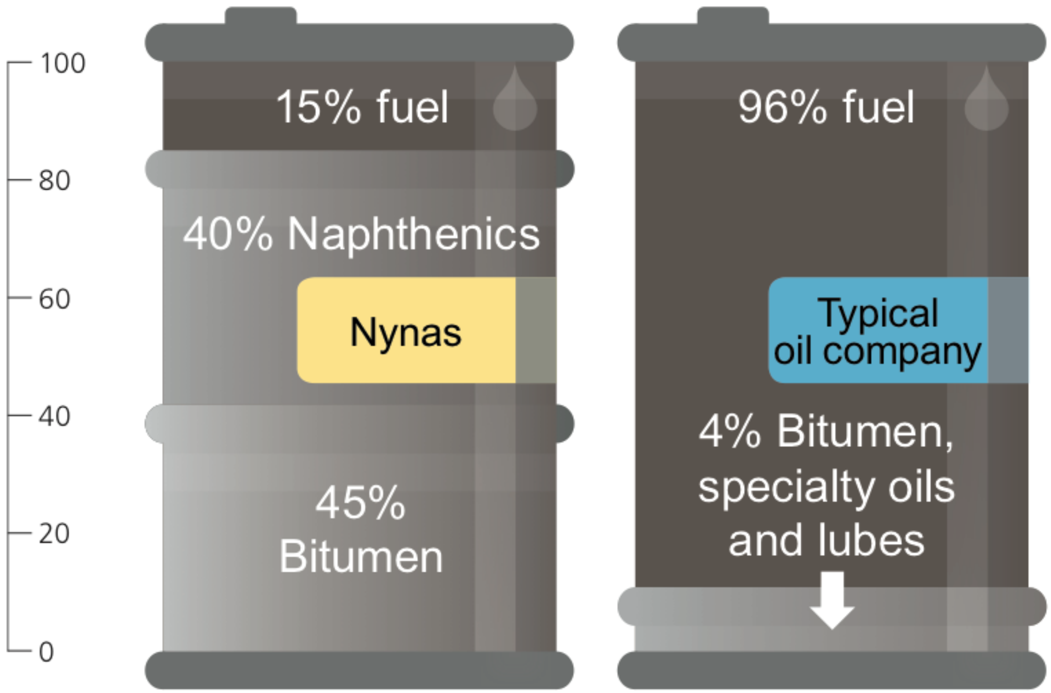
- Nynas is the largest specialty oil producer in Europe
- Offices in more than 30 countries around the globe
- Net Sales: 2 Billion USD (2015)
- Average number of employees: 1000
- Refineries in Nynäshamn (SE), Harburg (DE), Isla JV (Curacao), Eastham JV (UK), Antwerp JV (BE), Gothenburg (SE)

Nynashamn

Harburg

Nynas: The Different Oil Company

Typical
oil company



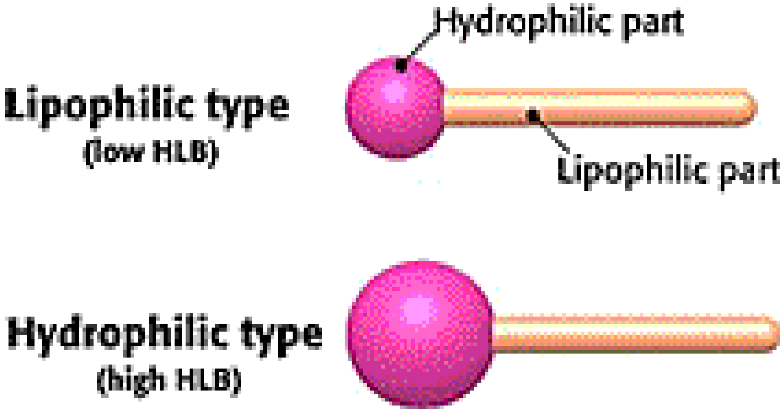
96% Fuel

4% Bitumen,
Specialty oils
and Lubes

A Metalworking Emulsion Fluid Stability Study

A metalworking fluid emulsion study

- Emulsion stability is key to MWF usefulness
  - Investigate the relationship between formulation and emulsion stability
- Water Hardness (°dH)
  - Investigate the influence of hard water on emulsion stability
- Base oil type selection
  - Which properties differ? Who does this matter?
- Emulsifier (surfactant) type and Hydrophile-Lipophile Balance (HLB)
  - How surfactant chemical properties limiting emulsion stability?



Base oil and water hardness selection

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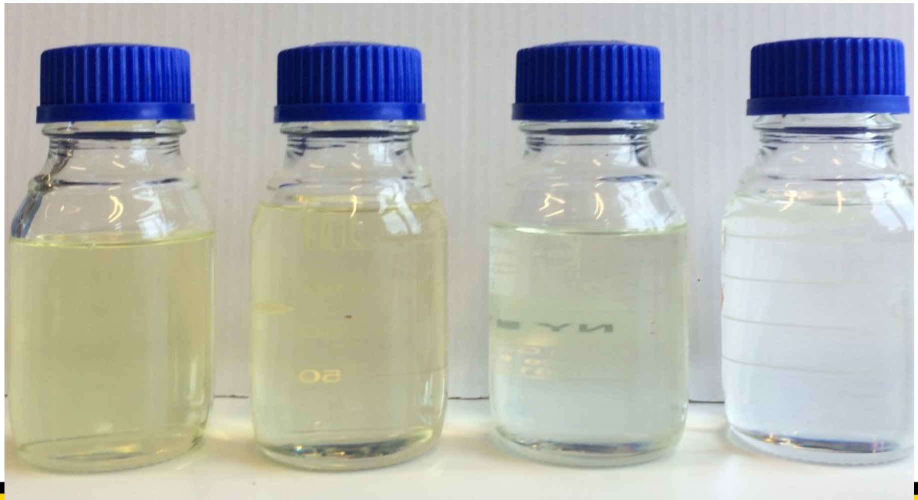
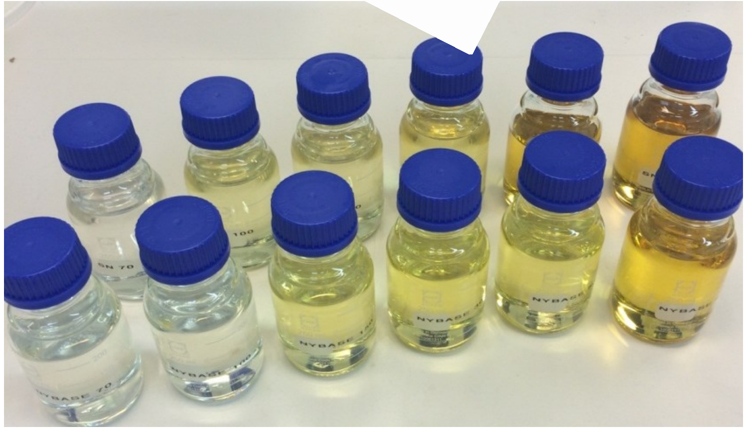


A new specialty base oi' product range

- Can be widely applied in inc… …nt formulations
- Naphthenic + Paraffinic bl…

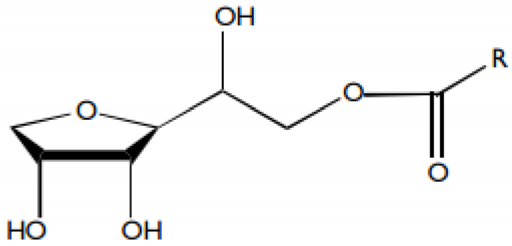
- Main advantages of the New …
  - Most similar base oil compareu…
  - High degree of flexibility in blending
  - Will be available over time
  - Superior low temperature performance

- Main challenges vs Group I base oils
  - Slightly higher volatility
  - Lower flash point
  - Slightly lower VI
  - Lower Sulphur content

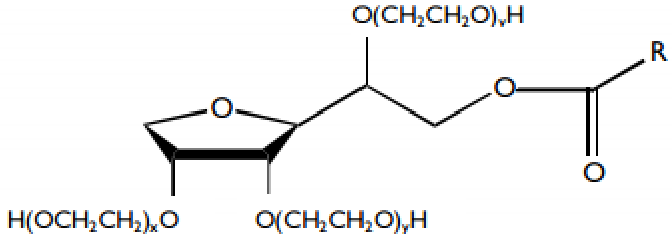


Emulsifier selection

- Emulsifiers (Surfactants)
  - **Span 80** (Sorbitan monooleate), HLB 4.3, Lipophilic



  - **Tween 80** (Polyethylene glycol sorbitan monooleate), HLB 15, Hydrophilic



- One commercially available emulsifier additive package
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  - Butyldiglycol

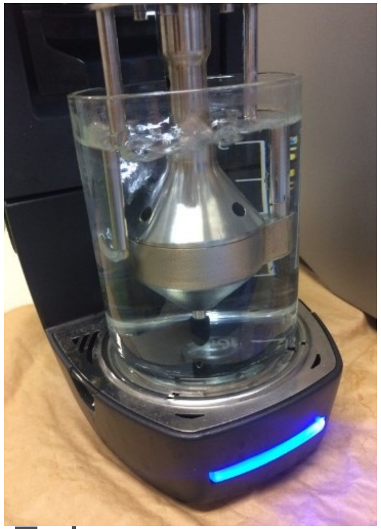
Emulsion stability determination

- We utilized two complementary approaches
- **1. Droplet Size Distribution (DSD)**
  - Determined at high dilution
  - Distribution changes over time
  - Coalescences can be detected
- **2. Light transmission and back scattering**
  - Determined "as-is" on the real liquid systems
- Emulsion stability is correlated to the growth of droplet size by coalescence
- Emulsion stability can be directly assessed by light scattering and vertical scanning
  - Sedimentation, creaming, layering etc can be observed directly and plotted time-resolved
  - Relation b/w different experiment through calculations

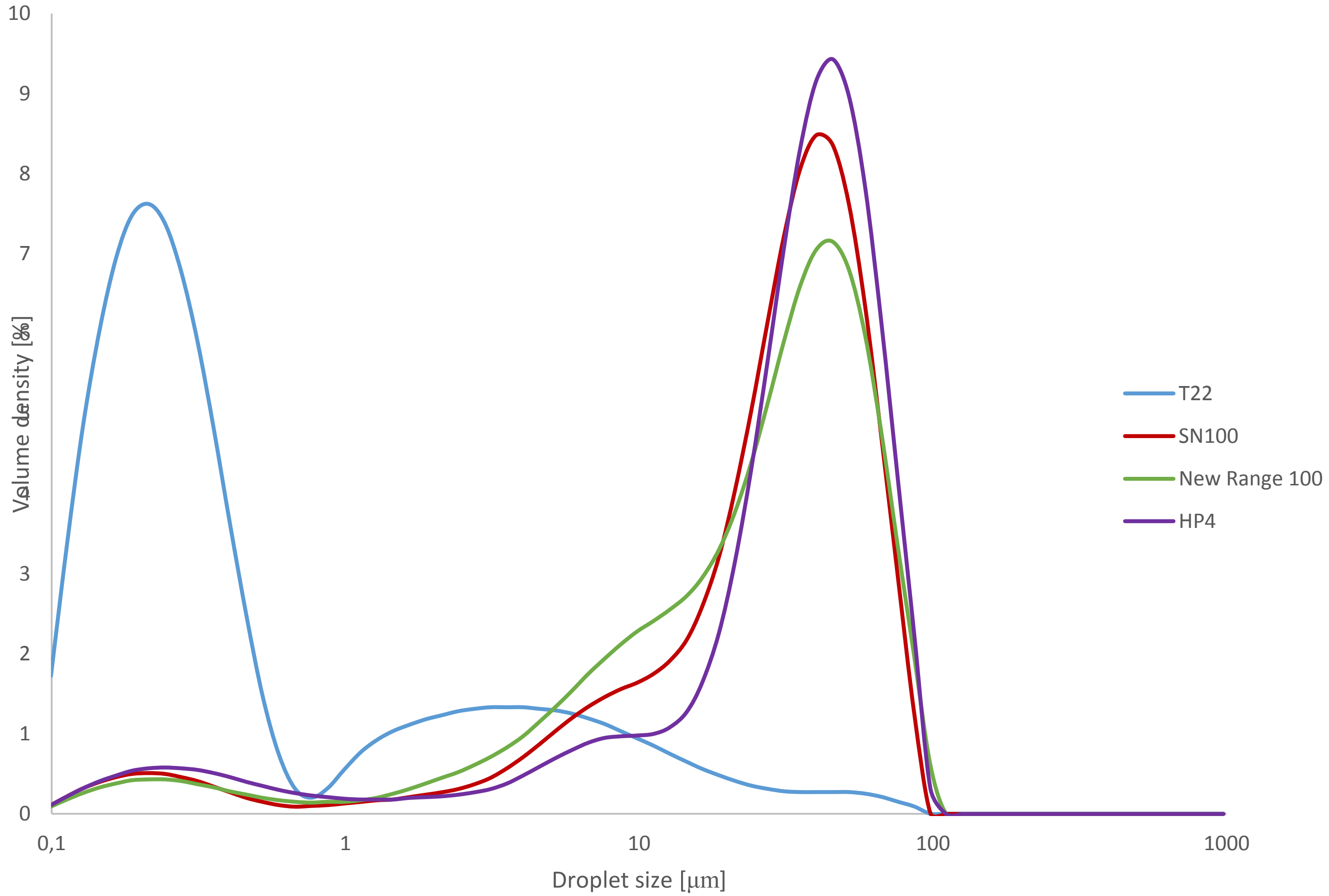
Droplet size distribution experiments

Methodology: Droplet size distribution experiments

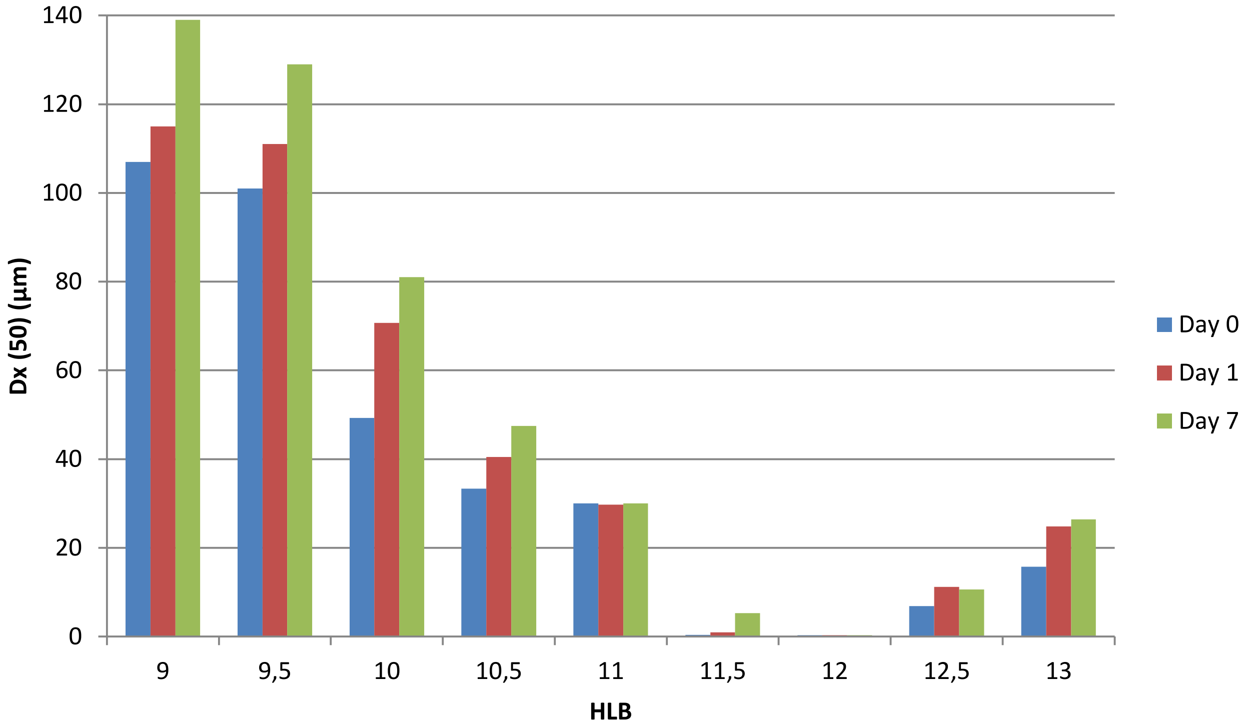
- Emulsions were formed, based on the four base oils
  - T 22, SN 100, New Range 100 & HP 4 Group II
- Span 80/Tween 80 blends
  - HLB range from 9 to13
- Water hardness, soft or hard
  - Soft water (°dH 0)
  - Synthetic hard water (°dH 20)
- Conditions for emulsion formation
  - Mild agitation for 3 minutes
  - 18 samples per base oil
- Emulsion droplet size distribution determined at t =0, 1 and 7 days
  - Malvern Mastersizer 3000E, measurements at high dilution



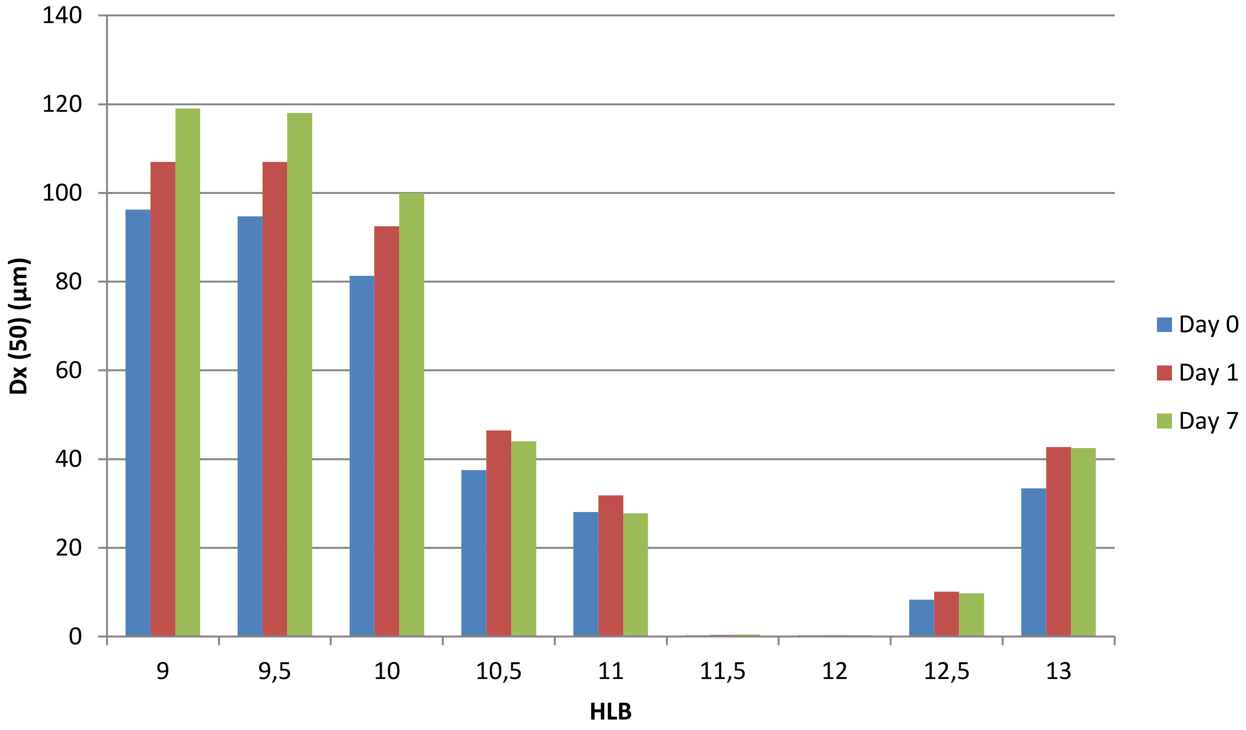
Droplet Size Distribution @ HLB 12, °dH 0



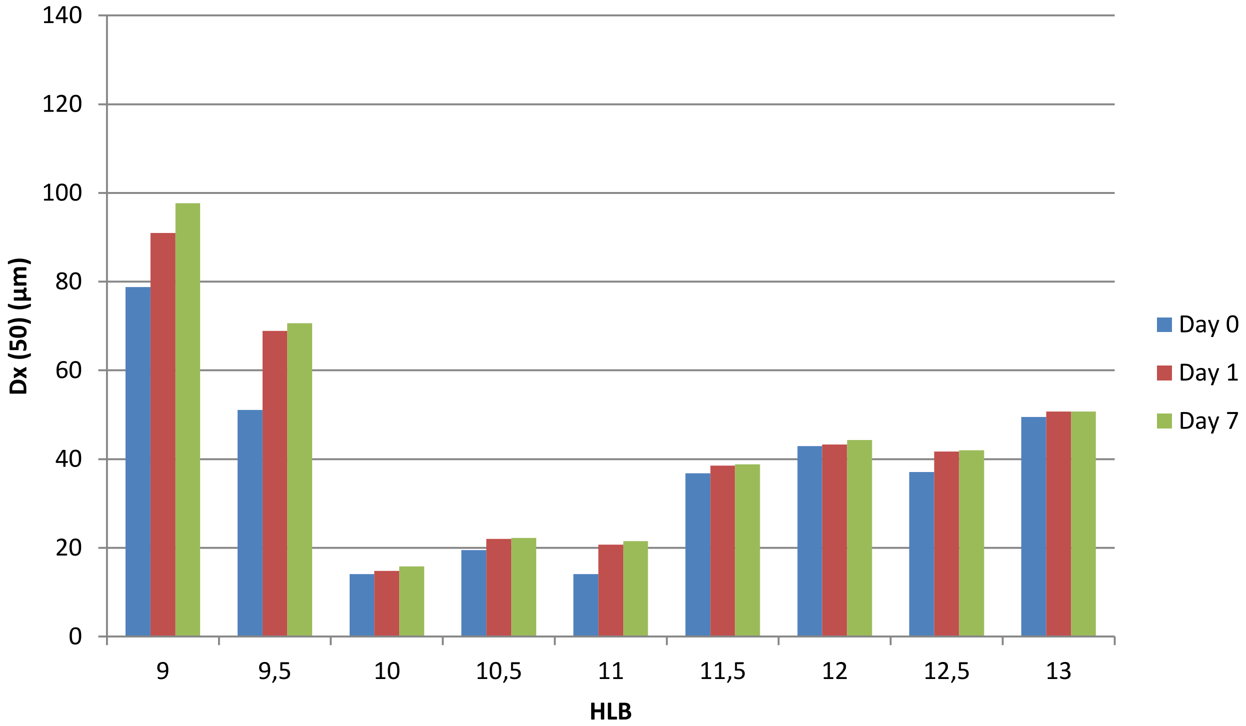
T22 in soft water (°dH 0)



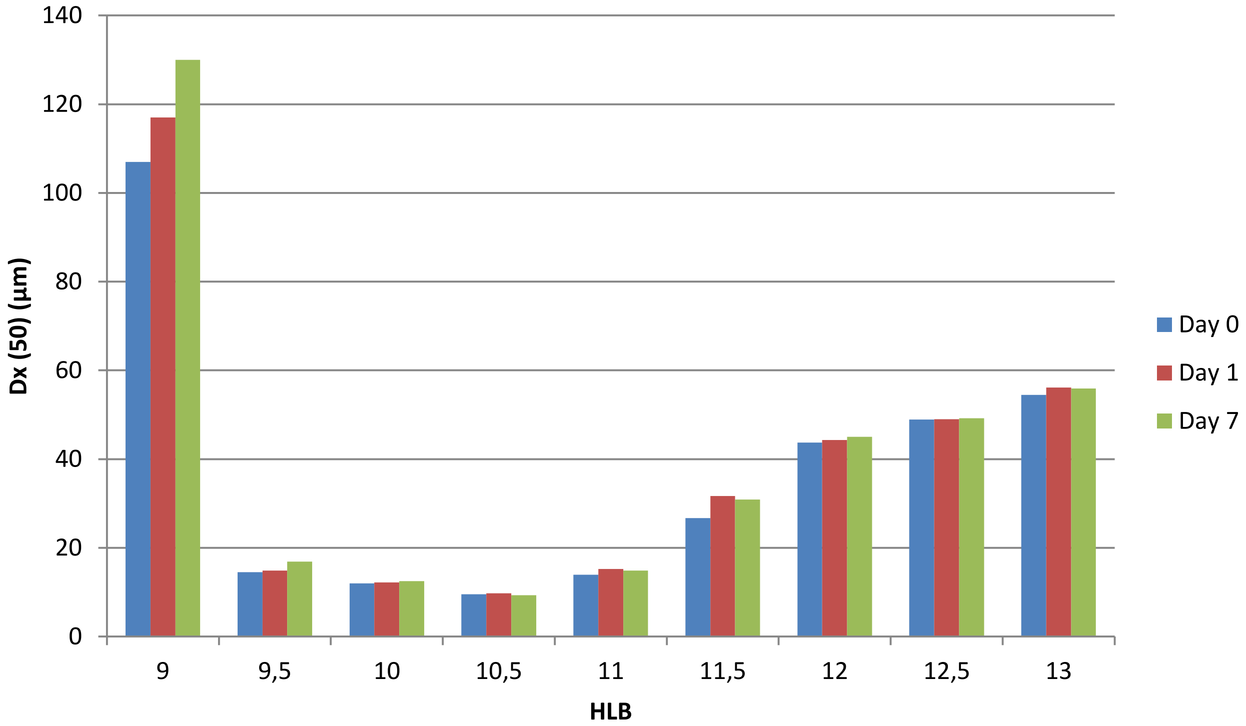
T22 in hard water (°dH 20)



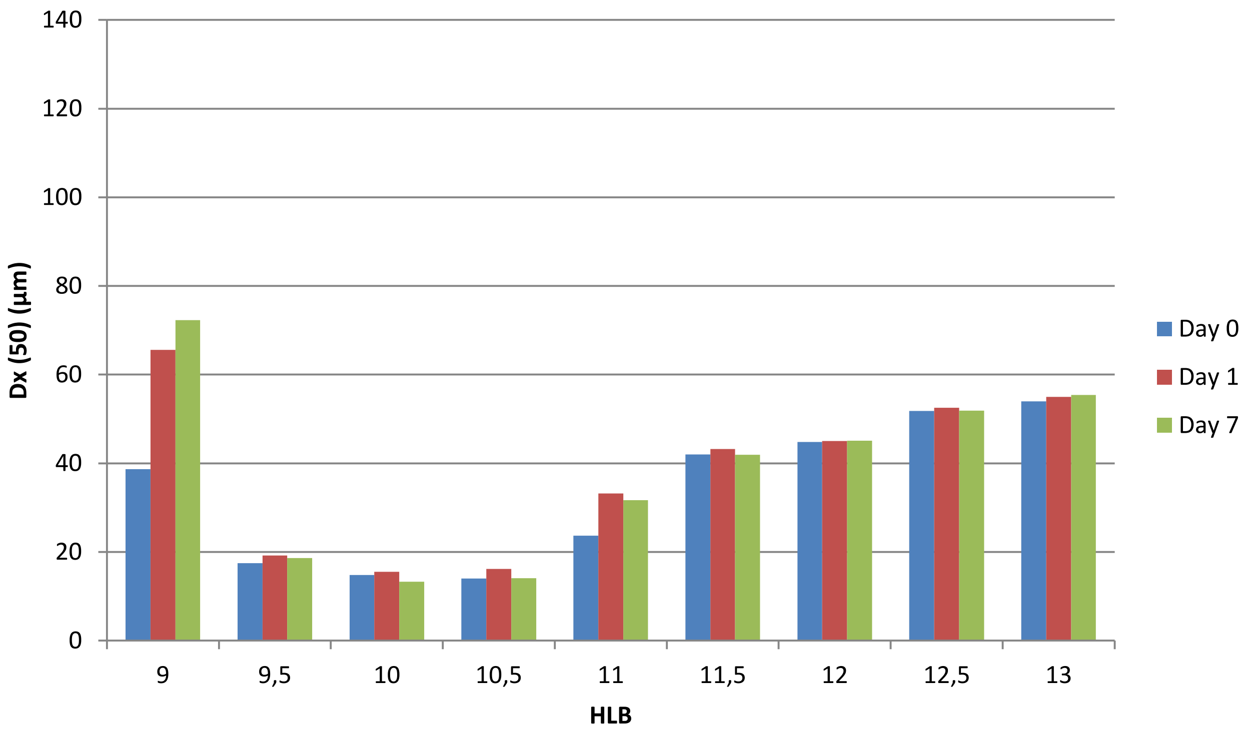
SN100 in hard water (°dH 20)



New Range 100 in hard water (°dH 20)



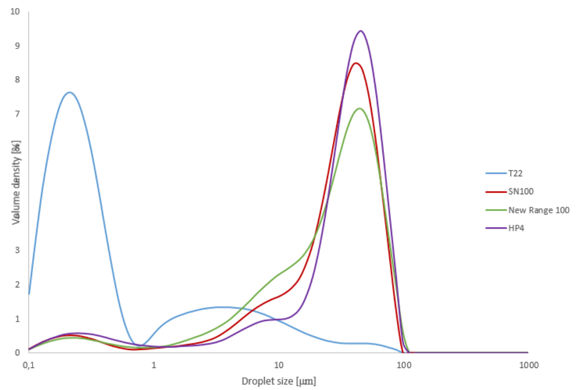
HP 4 in hard water (°dH 20)



Results and conclusion of DSD series

- Water hardness was not found to be of major impact
- Clear minimum value of droplet size could be determined
- The trend of coalescence (droplet mean size growth) can be observed over the one week measurement period
- An order of merit was observed for this emulsifier system:
- Naphthenic > Group I > Group II
  - This follows the solvency properties by Aniline Point order for these base oils

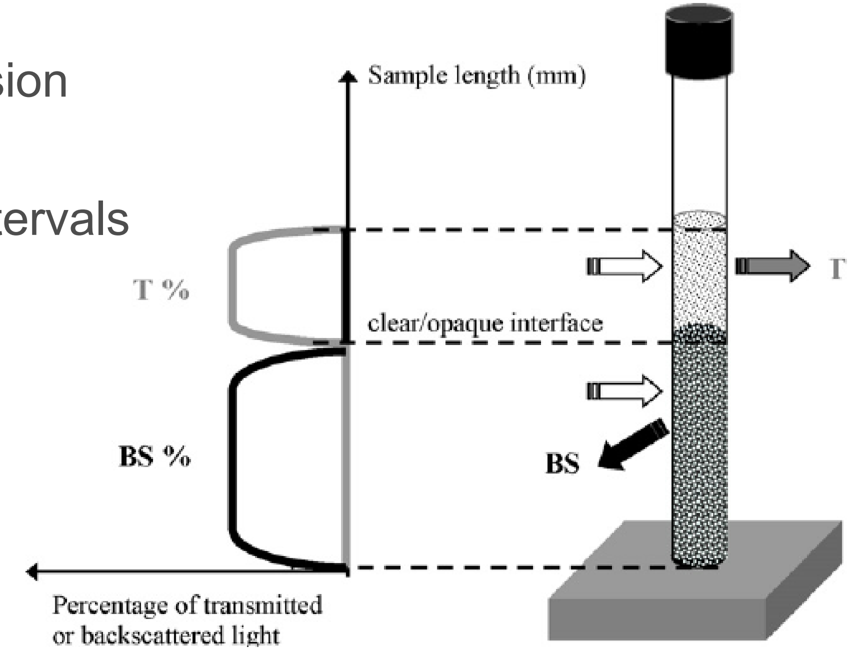
Droplet Size Distribution @ HLB 12, °dH 0

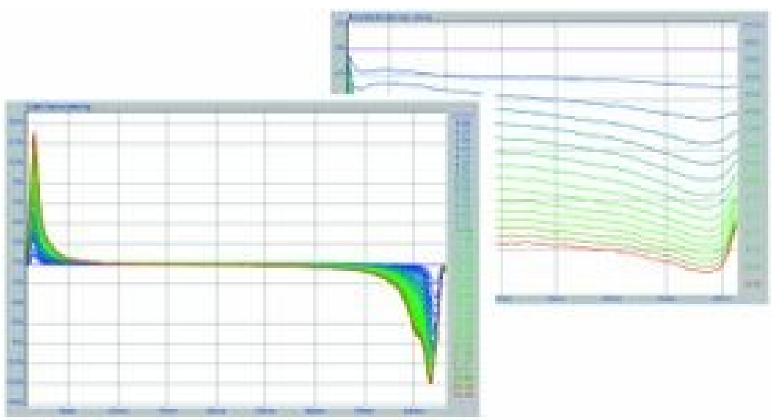


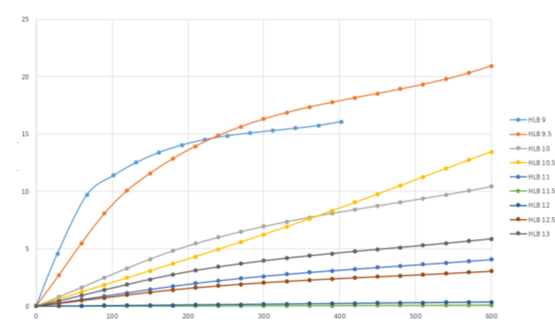
Emulsion phase thickness determination

Emulsion phase stability and thickness

- Principle: light back scattering or transmission
- Scan from bottom to top of sample volume
- Sweep curves obtained at different time intervals
- Analytical software determines TSI
  - TSI= Turbiscan Stability Index
  - The overall picture in a number



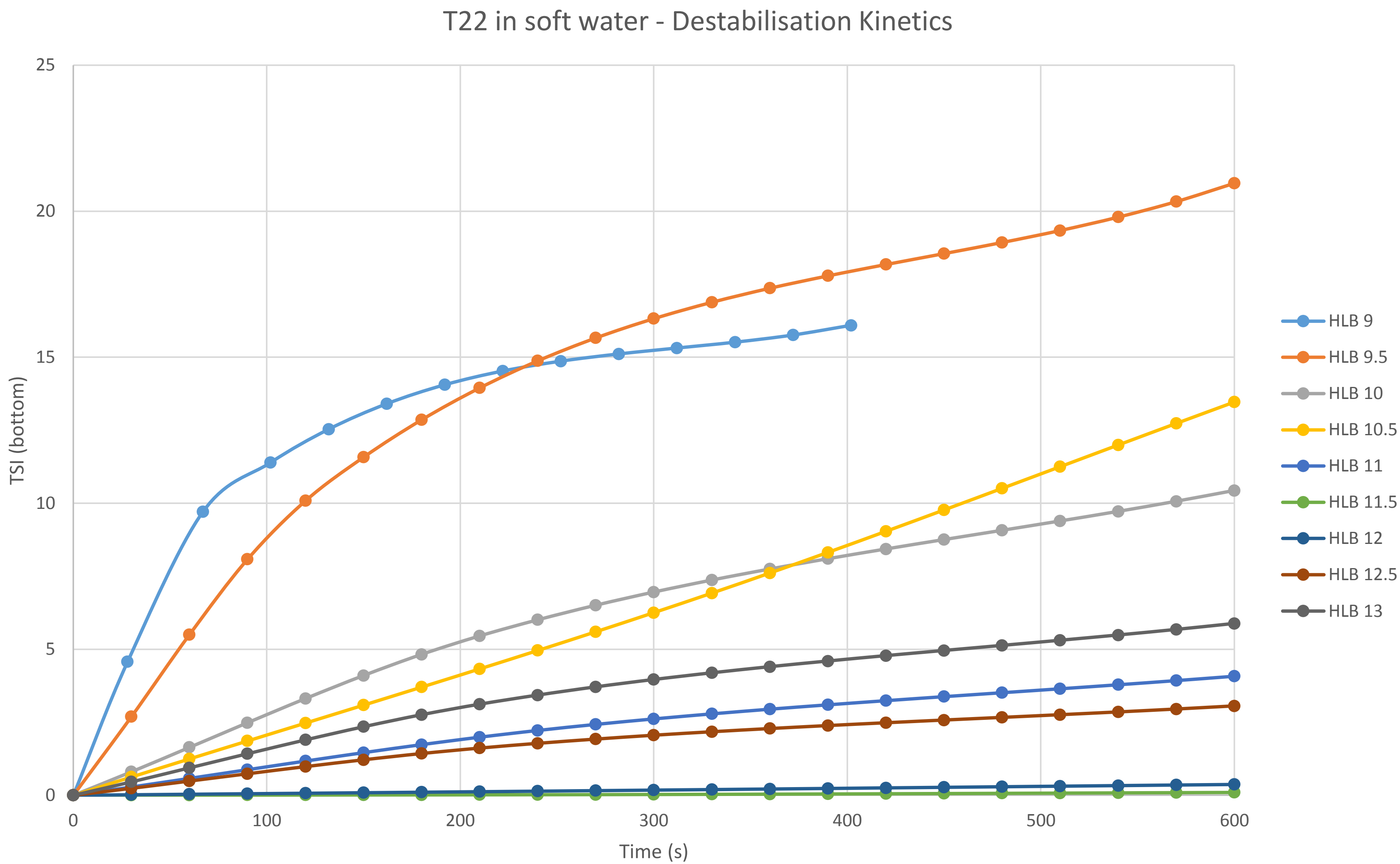




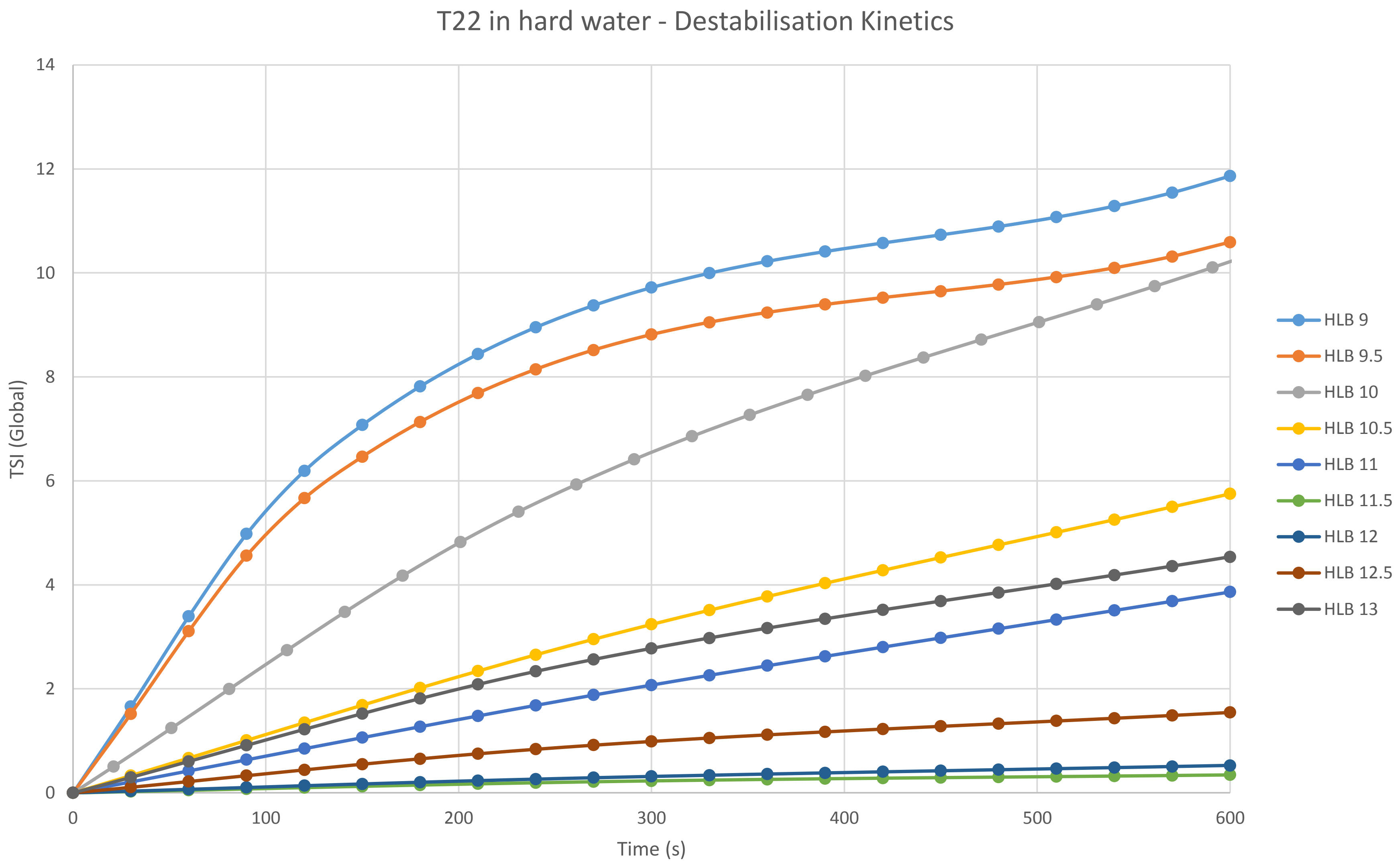
Methodology: Emulsion phase stability determination

- Emulsion phase destabilisation kinetics determination
- Emulsions were formed, based on the four base oils
  - T 22, SN 100, New Range 100 & HP 4 Group II
- Span 80/Tween 80 blends
  - HLB range from 9 to13
- Water hardness, soft or hard
  - Soft water (°dH 0)
  - Synthetic hard water (°dH 20)
- Conditions for emulsion formation
  - Mild agitation for 3 minutes
- 18 samples per base oil
- Emulsion phase stability determination by destabilisation kinetics at t =0, and every 30 s up to ten minutes
  - Turbiscan LAB , measurements at actual concentration "as-is"
    - Instrument loan kindly provided by Gammadata, Sweden

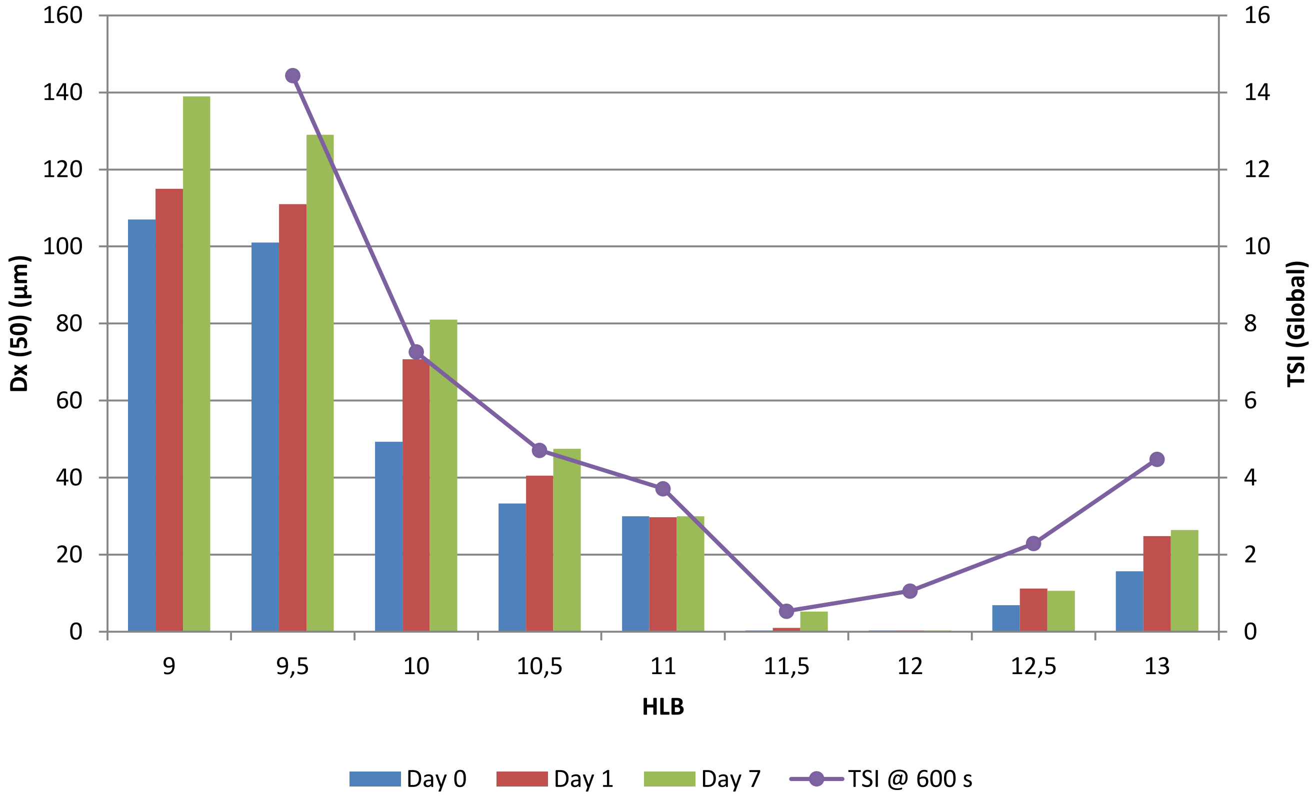
T22 in soft water - Destabilisation Kinetics



T22 in hard water - Destabilisation Kinetics



DSD and TSI co-variation, T 22 in soft water



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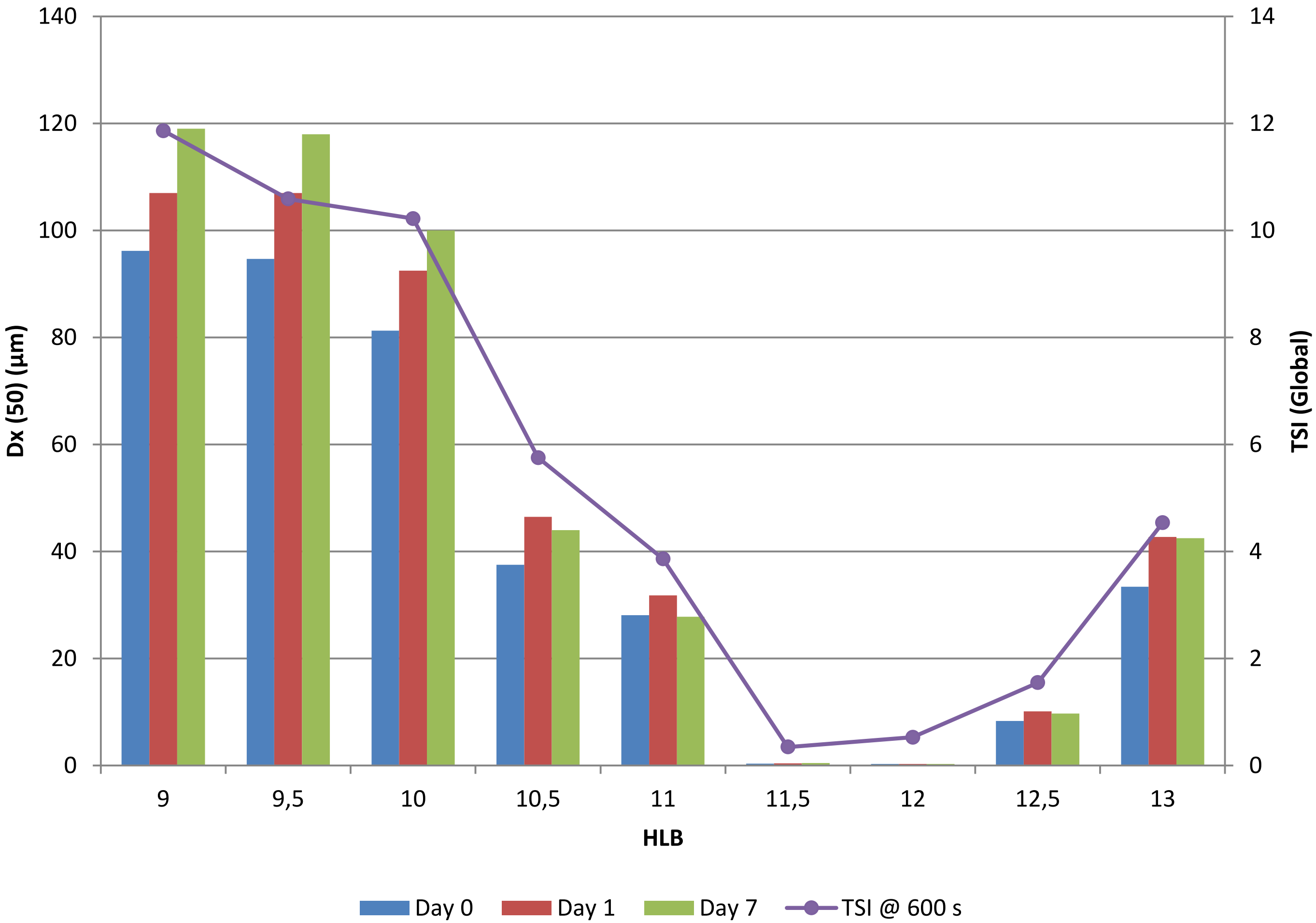
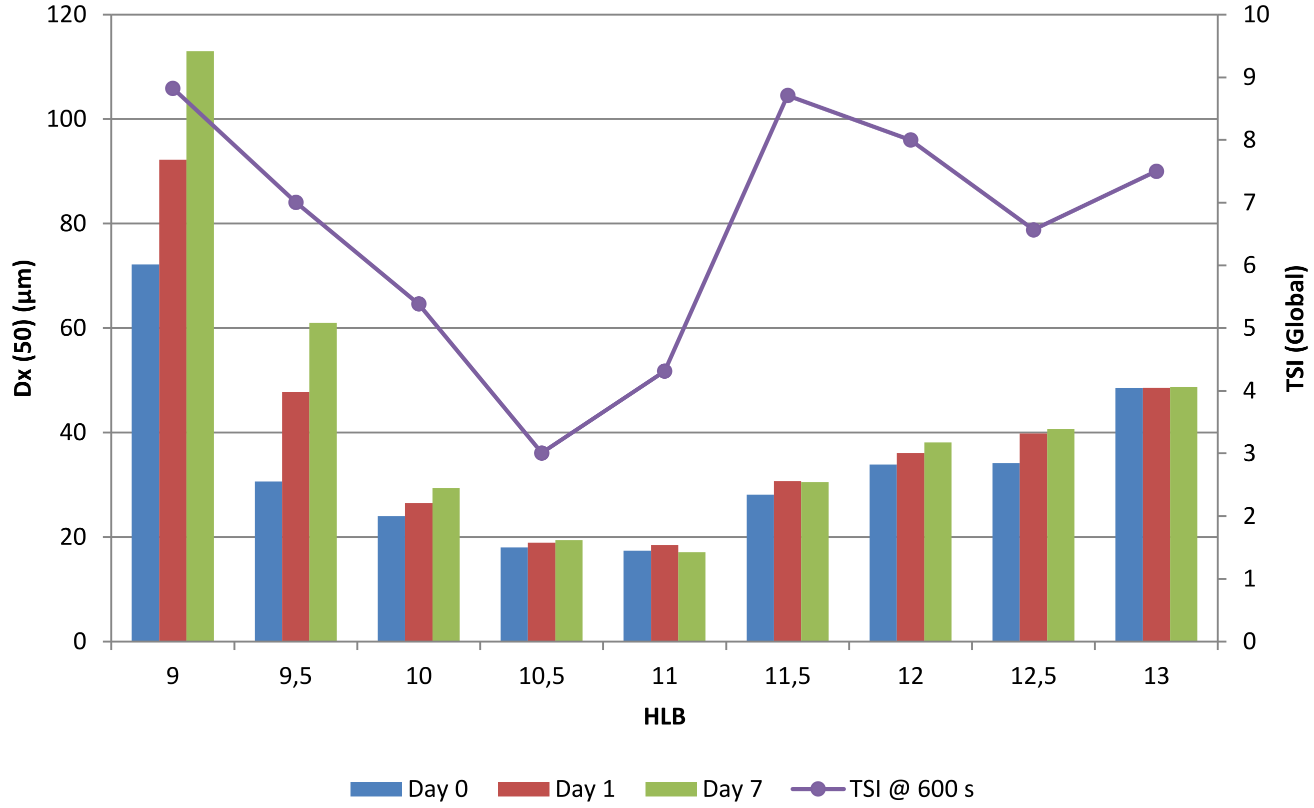
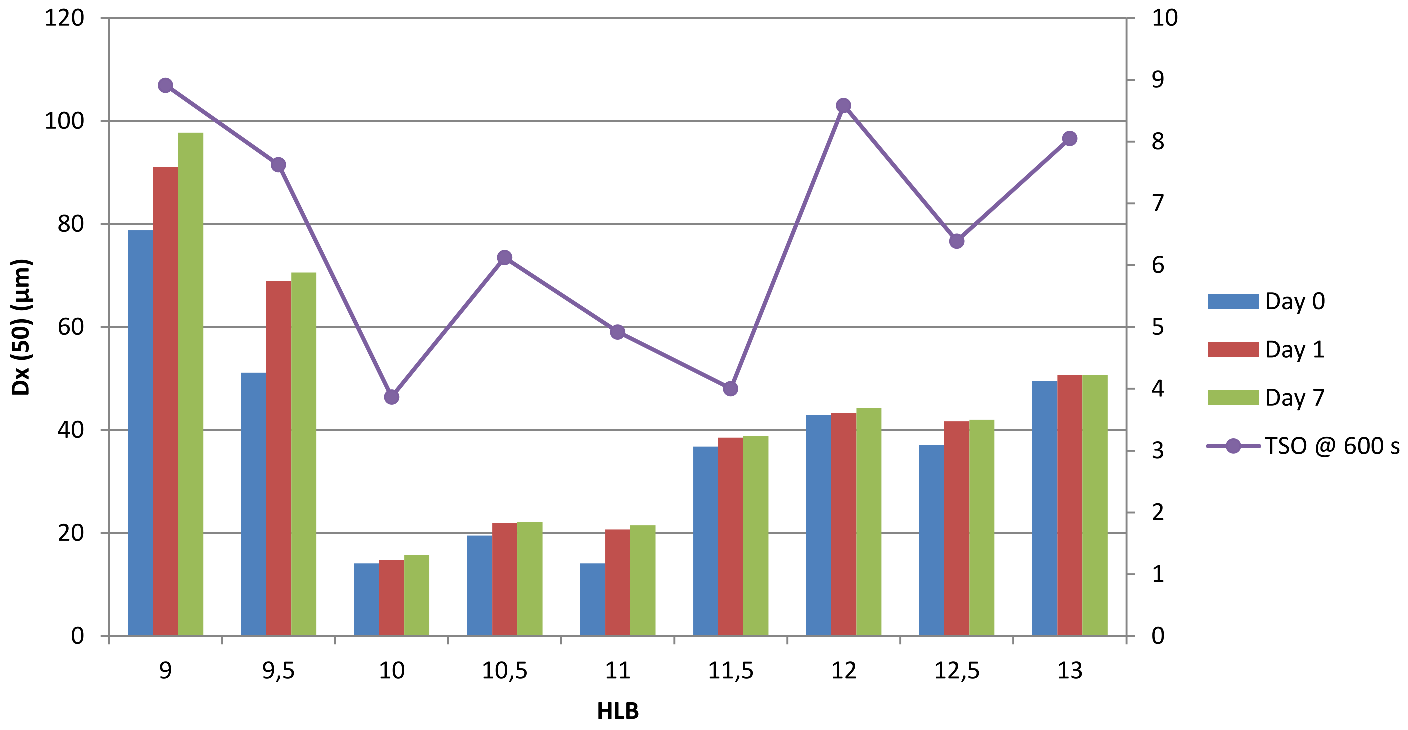


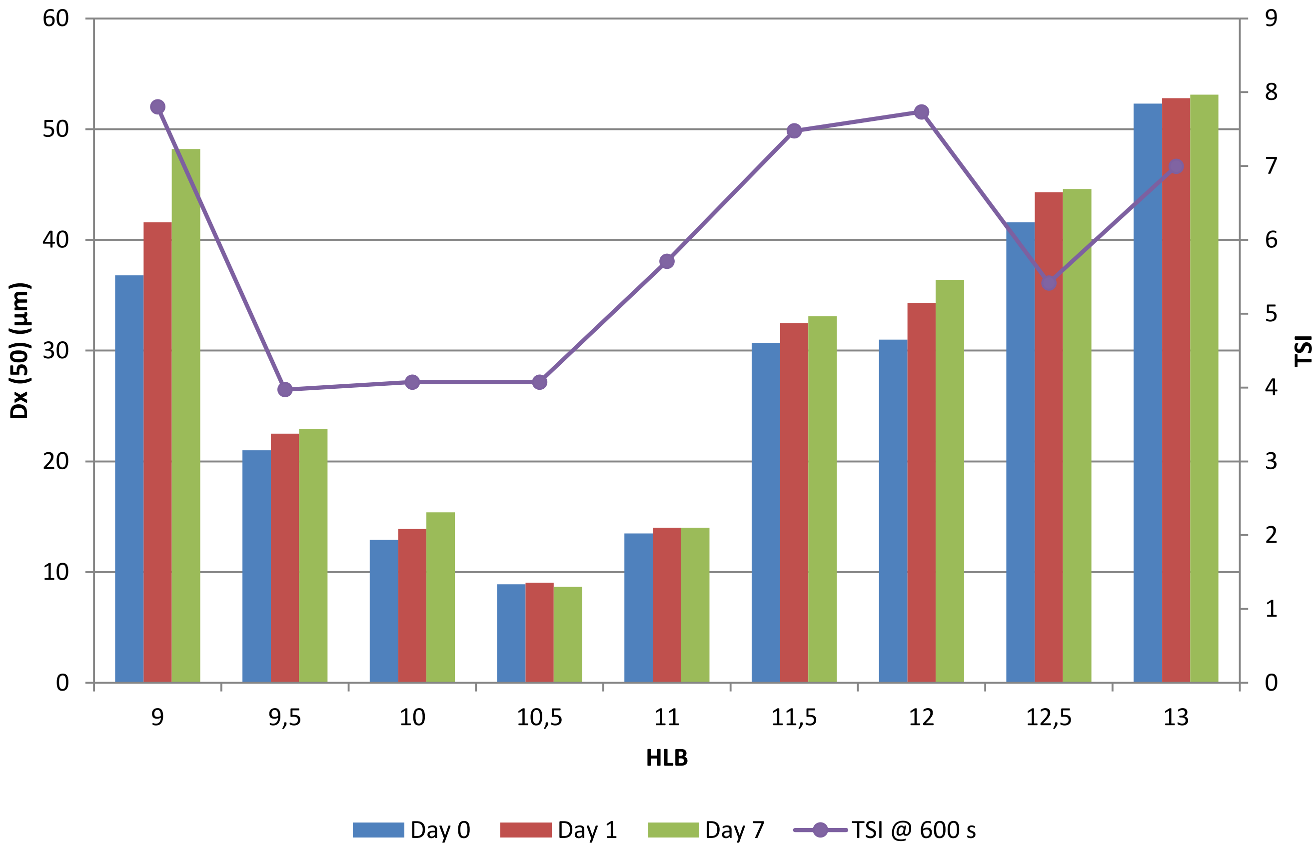
DSD and TSI co-variation, SN 100 in soft water



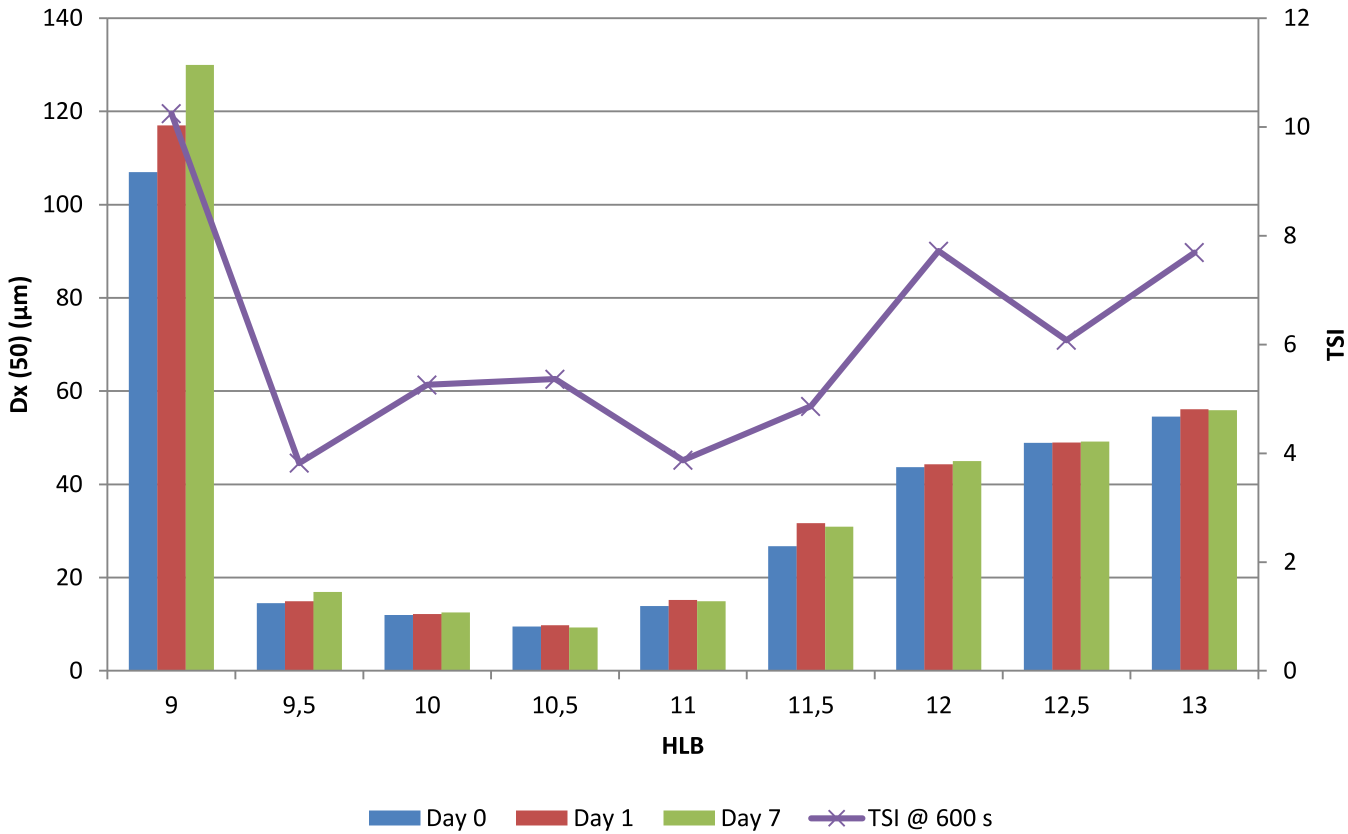
DSD and TSI co-variation, SN 100 in hard water



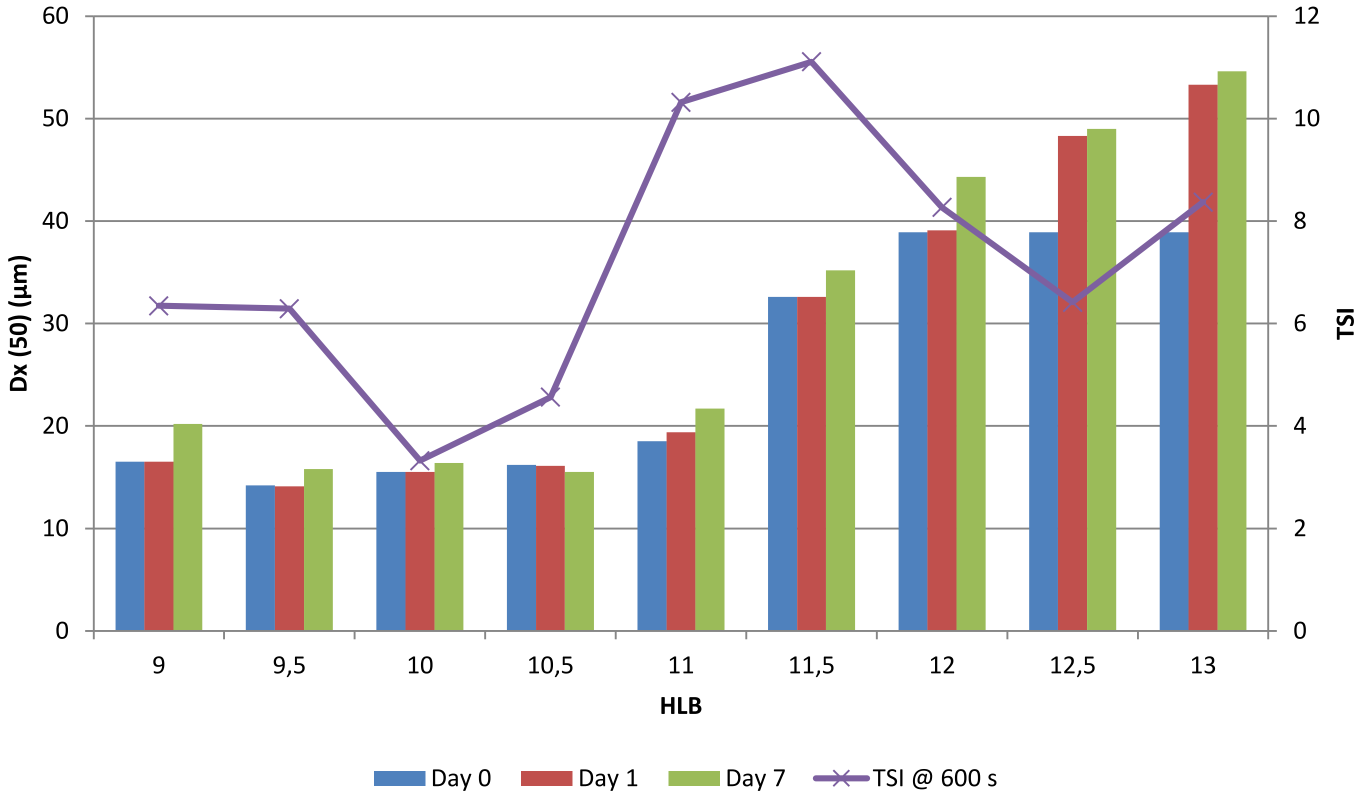
DSD and TSI co-variation, NR 100 in soft water



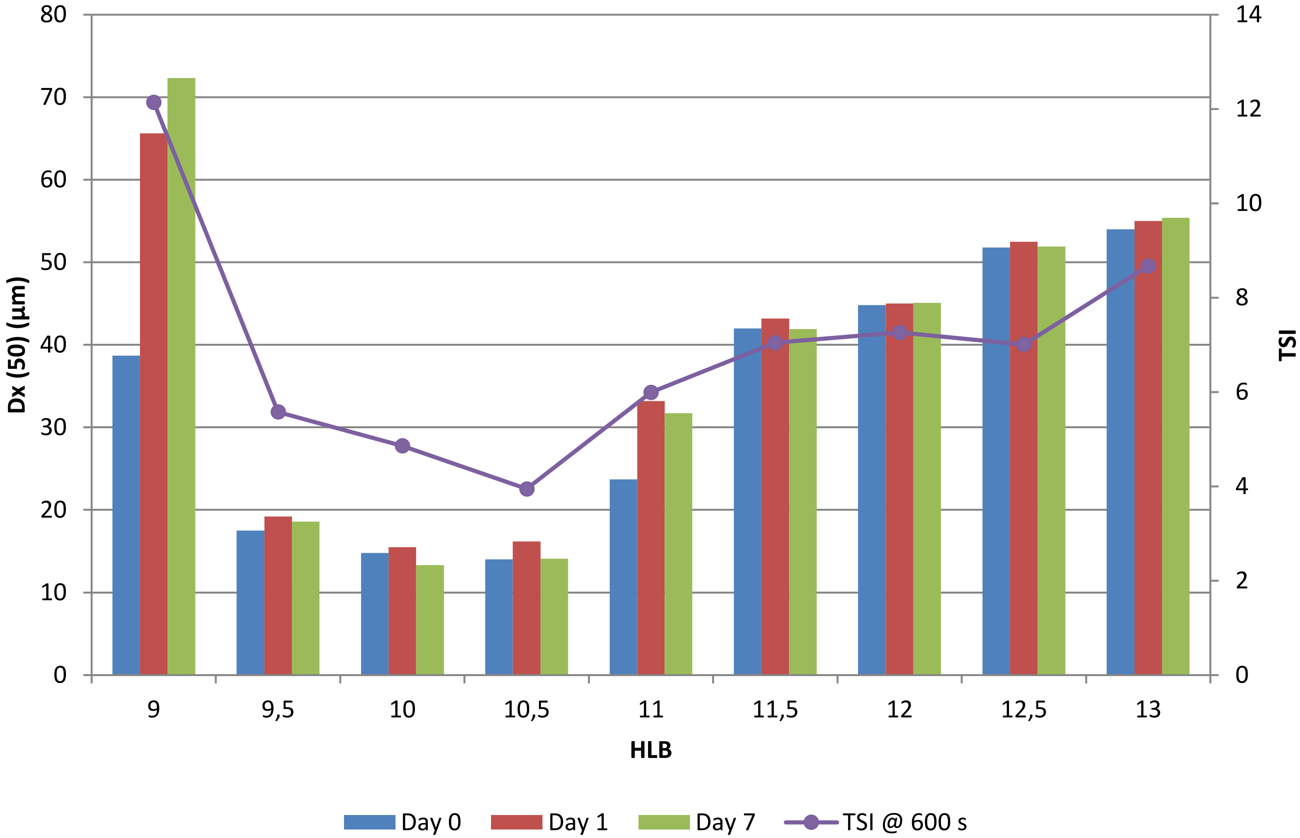
DSD and TSI co-variation, NR 100 in hard water



DSD and TSI co-variation, HP 4 in soft water

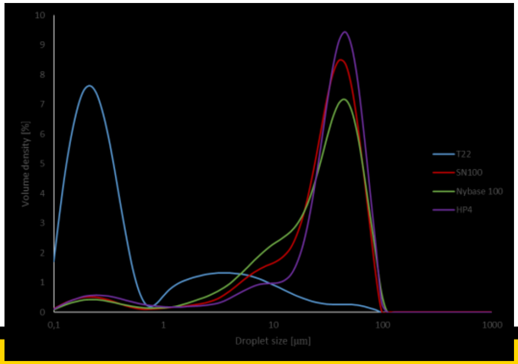


DSD and TSI co-variation, HP 4 in hard water



Results and conclusion of DSD vs phase thickness (destabilisation kinetics by TSI)

- Water hardness not of major impact
- In the Tween/Span emulsifier system, a clear minimum value of droplet size could be determined
- The trend of coalescence can be observed over the one week measurement period
- The correlation b/w DSD and TSI is ***best*** for the very stable emulsions, e.g. naphthenic base oil systems
- The correlation becomes ***weaker*** for the systems that do not display very small DSD (ca. 1 µm), but where DSD is between 10 and 20 µm at best
- The two methods correlate in principle
- The emulsion thickness method intuitively is closer to the real and observable emulsion fluid systems



Reference case 1: emulsion stability results with a commercial emulsifier package

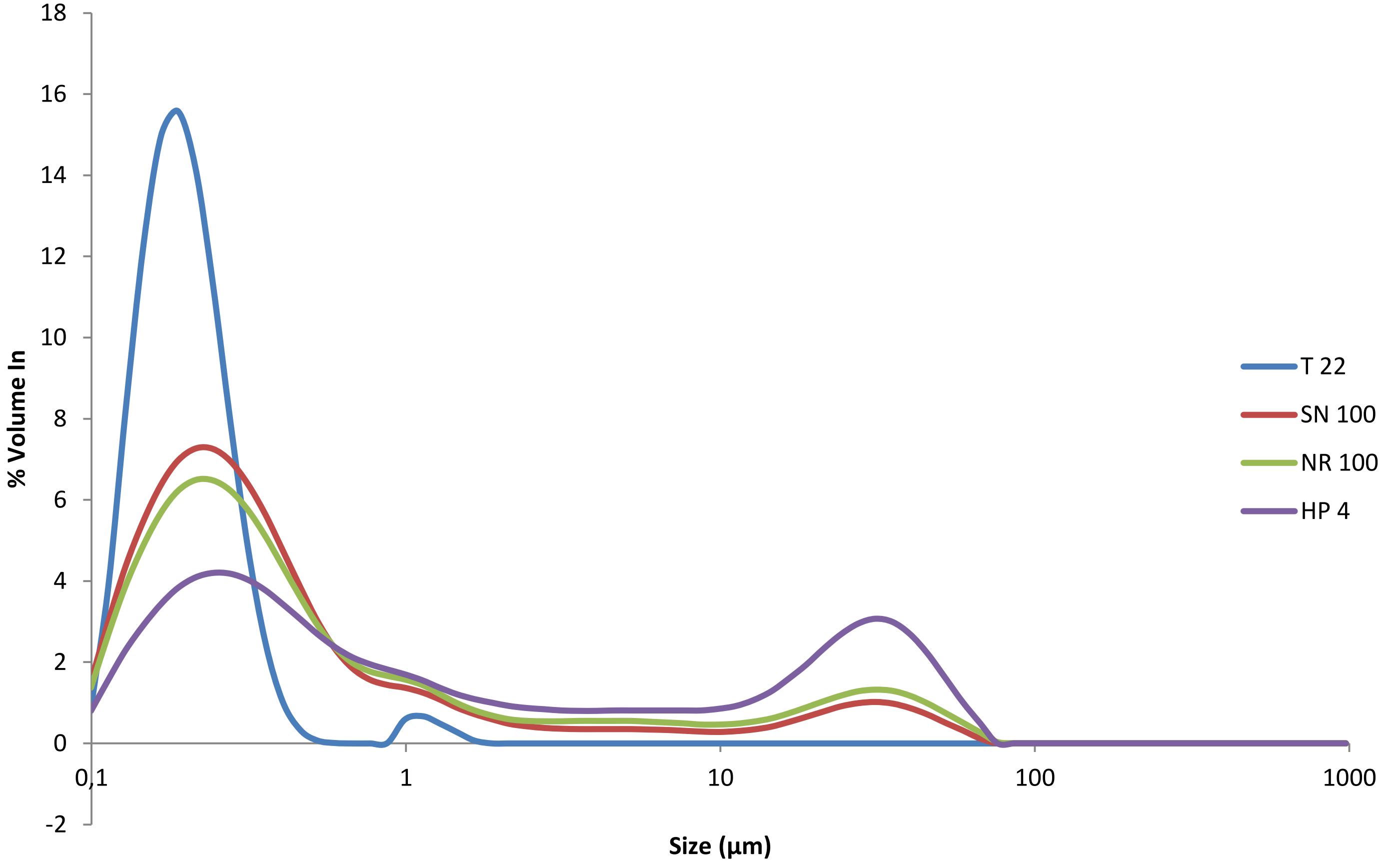
- Droplet Size Distribution (DSD) determination
- Emulsions were formed, based on the four base oils
  - T 22, SN 100, New Range 100 & HP 4 Group II
- One commercially available emulsifier package
  - A newly developed range of non-ionic emulsifiers from Solvay
  - HLB value 8.5 (optimized for Naphthenic base oil)
    - NB! HLB for this system is not necessarily comparable to the HLB dependence established for the Tween/Span system
- Water hardness, soft or hard
  - Soft water (°dH 0)
  - Synthetic hard water (°dH 20)

Reference case 1: emulsion stability results with a commercial emulsifier package

- Conditions for emulsion formation
  - Mild agitation for 3 minutes
  - Two samples per base oil
  - Eight in all

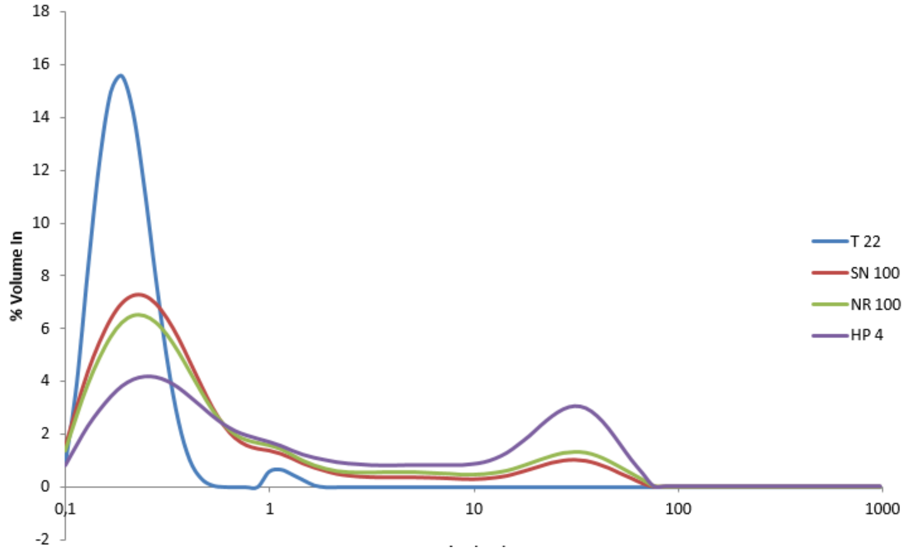
- Droplet Size Distribution (DSD) determination at t = 0, 1 and 7 days

DSD for Commercial emulsifier package in soft water, t=0



Reference case 1: DSD results

- The naphthenic base oil displays a clear maximum DSD at ca 0.5 µm
- The paraffinic Group I and Group II base oils display a two-phase DSD behaviour, with a second stability maximum cantered around 60 µm droplet size



- We could not detect any significant droplet size distribution change over the test duration
- A commercial formulation could reasonably be expected to show emulsion stability over longer times

Reference case 2: emulsion stability results with a commercial emulsifier package

- Emulsion phase destabilisation kinetics determination
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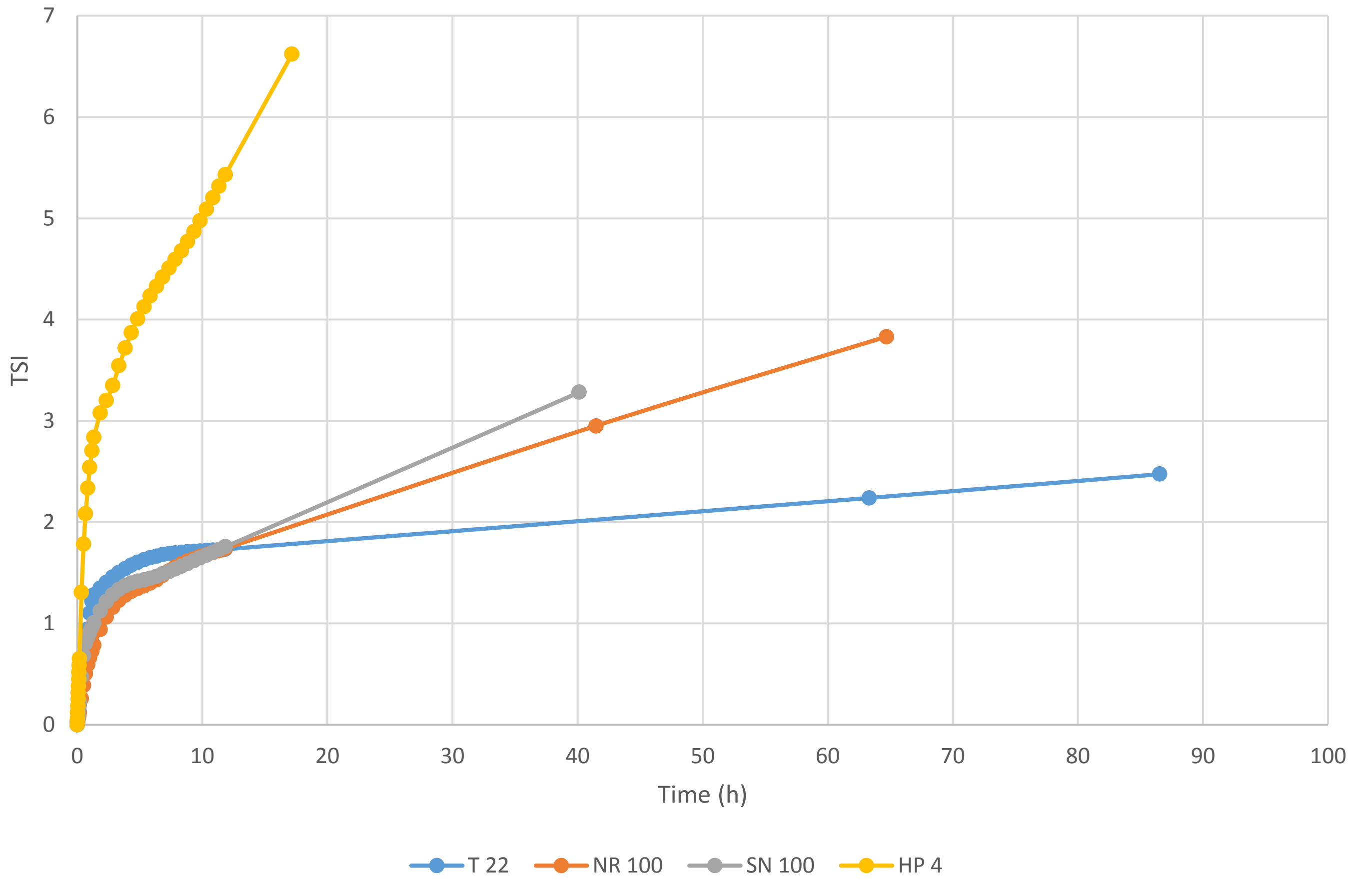
  - HLB value 8.5
    - NB! HLB for this system is not necessarily comparable to the HLB dependence established for the Tween/Span system
- Water hardness, soft or hard
  - Soft water (°dH 0)
  - Synthetic hard water (°dH 20)

Reference case 2: emulsion stability results with a commercial emulsifier package

- Conditions for emulsion formation
  - Mild agitation for 3 minutes
  - Soft water (°dH 0)
- Emulsion phase thickness determination at t = 0, up to ten (10) hours at increasing intervals
- Data was collected also after 1, 2, 3 & 4 days (until TSI 3 was reached)
  - Turbiscan LAB , measurements at actual concentration “as-is”

Destabilisation kinetics by TSI



Results and conclusion of DSD vs phase thickness (destabilisation kinetics by TSI)

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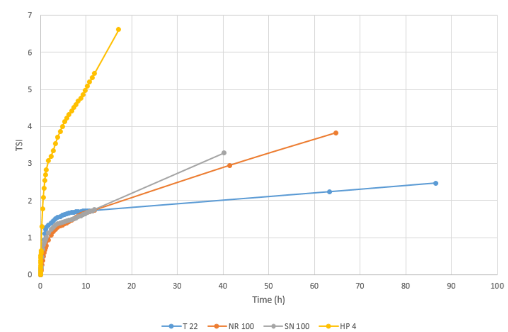
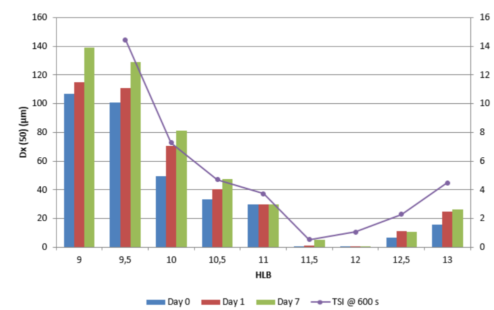
Destabilisation kinetics by TSI



DSD and TSI co-variation, T 22 in soft water



Summary and conclusions

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- Emulsion stability can me modelled in test systems
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- The droplet size distribution (DSD) method offers a wealth of data, and can generate a well-resolved mapping of the stability properties
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- The solvency, as indicated by the aniline point, mirror this order, and thus might play an important role for emulsion stability in the systems investigated

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