Compatibility of Nonionic Surfactants with Membrane Materials and their Cleaning Performance

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Membrane types, materials and uses

- Micro Filtration
- Ultra Filtration
- Nano Filtration
- Reversed Osmosis
- Polyethersulfone
- Polyamide
- Polyvinylidene difluoride
- Polyacrylonitrile
- Cellulose Acetate

- Waste water treatment
  - Paper industry
- Production process
  - Dairy industry
  - Breweries
  - Pharmaceutical industry
- Desalination of seawater
Cleaning of Membranes

- After a certain time of operation, membrane permeability starts to drop
- Reason is adsorption of inorganic and organic matter on the membrane surface (scaling, biofouling)
- One or more cleaning steps are necessary to regain the original membrane permeability
- To remove scaling, acids, chelates and polymers are used
- To remove biofouling, often caustic, oxidants and surfactants are used
- All cleaning steps take time and reduce thereby the output/production

→ Need for fast and efficient surfactants
Currently only few types of surfactants are used in membrane cleaning, mainly

- LAS (linear alkylbenzene sulfonate)
- Triton X-100 (iso-octylphenol ethoxylate, 9.5 EO)

The disadvantages of these surfactants are foam or environmental issues.

In a general assumption other nonionic surfactants than alkyl phenol ethoxylates have the tendency to adhere to the membrane material and thereby clog the pores.

Most membrane manufacturers forbid the use of nonionic surfactants by declaring a loss of the guarantee.

Need for low-foaming, non-adhering, biodegradable surfactants.
Sample preparation

- The membrane materials PES (polyethersulfone), respectively PA (polyamide 12) were spin coated on silicon wafers or glass plates.

- The thickness was analysed by ellipsometry based on the difference of the refractive indices.

- The thickness of the polymeric material was approx. 30 nm.
Adsorption/Desorption Measurements

- The coated wafers were dipped for 10 minutes in a 0.025% surfactant solution, rinsed with water and dried.
- This procedure was repeated 4 times
- The thickness of the resulting layer was determined with a quartz microbalance
## Products used

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
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<tbody>
<tr>
<td>Triton® X-100</td>
<td>Octylphenol ethoxylate</td>
<td>LAS</td>
<td>Linear alkylbenzene sulfonate</td>
</tr>
</tbody>
</table>

For the Lutensol® XL, XP and XA types the first number indicates the amount of EO units (i.e. 50 means 5 EO units), for the Lutensol® TO types, A types and Emulan® AT the number indicates the amount of EO units. Triton® X-100 was purchased from DOW, subtilisin from Sigma-Aldrich. Lutensol®, Dehydol®, Plurafac®, Dehypon®, Emulan® and Trilon® are trademarks of BASF SE.
Remaining Thickness of various Surfactants on Polyamide

Thickness [ng/cm²]

- Triton X-100
- Lutensol XL 50
- Lutensol XP 60
- Lutensol XA 60
- Lutensol XA 40
- Lutensol XA 60
- Lutensol TO 60
- Lutensol TO 80
- Lutensol TO 90
- Lutensol TO 100
- Lutensol TO 120
- Lutensol TO 3
- Lutensol TO 5
- Lutensol TO 7
- Lutensol TO 90
- Lutensol TO 100
- Lutensol TO 120
- Lutensol TO 150
- Lutensol TO 180
- Lutensol TO 200
- Lutensol TO 250
- Lutensol TO 300
- Lutensol TO 400
- Lutensol TO 500
- Lutensol TO 600
- Lutensol TO 700
- Lutensol TO 800
- Lutensol TO 900
- Lutensol TO 1000

The information on this chart is patented knowledge.
Remaining Thickness of various Surfactants on Polyethersulfone

Thickness [ng/cm²]

The information on this chart is patented knowledge.
Biofouling Layers on PA and PES

- **desalination**-
  (polyamide)

  Bovine serum albumin (BSA), alginat (AG) and humic acid (HA)
  on **PA-layers**

- **food processing**-
  (polyethersulfone)

  Casein (CAS) and lactalbumin (LAC)
  on **PES-layers**
Cleaning Speed on PA-Layers

The information on this chart is patented knowledge.

Conc. 0,025%

pH 12
Cleaning Performance on PA-Layers

Conc. 0,025%
PH 12
10 min cleaning

The information on this chart is patented knowledge.
Cleaning Performance on PES-Layers

Conc. 0,025%

pH 8

10 min cleaning

the information on this chart is patented knowledge
Cleaning Performance of Lutensol TO Types (branched C\textsubscript{13}-alcohol ethoxylates)

HLB = 10 - 12

The information on this chart is patented knowledge.
Wetting of hard surfaces - Dynamic contact angle

- Contact angle measurement with high speed camera (360 pics / s)
- Young’s Law $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \Theta$
  controls wetting and spreading
- different types of surfaces can be used: glass, ceramics, steel, aluminum, copper, polyethylene, …
Dynamic contact angle of Lutensol TO types on PA

Time [s] vs. Contact angle [°]

- Water
- TO 3
- TO 12
- TO 5
- TO 8
- TO 7
- TO 6
Dynamic contact angle of Lutensol TO types on PES

Contact angle [°]

- Water
- TO 8
- TO 3
- TO 12
- TO 5
- TO 7
- TO 6

Time [s]

0.01  0.10  1.00  10.00
Cleaning Performance of Lutensol X Types (2-Propylheptanol alkoxylation)

HLB = 10 – 13
Extended surfactants

Cleaning [%]

Lutensol XP 30
Lutensol XL 40
Lutensol XA 40
Lutensol XL 50
Lutensol XA 50
Lutensol XL 60
Lutensol XA 60
Lutensol XL 70
Lutensol XL 80
Lutensol XL 90
Lutensol XP 60

ethoxylates
Validation of Test Method

Adsorbed BSA, AG, HA allow to test the stability of molecular fouling layers, but ...

... what about crosslinked matrix components?
Extension of the biofilm model - Marine biofilms (Cobetia marina)

- reproducible film formation on PA-layer
- quantification of cells and matrix: staining /spectroscopy
- analysis of layer morphology: AFM and SEM

01.04.2014
Comparison Test Model / Bacterial Layer

Surfactants remove bacteria but almost no matrix.
Exploration of cleaning mechanism
Extended AFM studies – single bacterial cell force spectroscopy

Nature Protocols 5, 1353–1361, Jens Friedrichs, Jonne Helenius & Daniel J Muller
Quantifying cellular adhesion to extracellular matrix components by single-cell force spectroscopy
Comparison Test Model / Bacterial Layer

Detachment Force [nN]

Cleaning [%]

Lutensol XL 60 lowers the adhesion most

the information on this chart is patented knowledge
Combinations of Cleaning Agents (surfactant – chelate - enzyme)

- Almost no removal of bacteria or matrix in phosphate buffer (pH 8.1)
- Efficiency of single cleaning agents: Subtilisin < Lutensol XL 60 < Trilon M
- Lutensol XL 60 + subtilisin: more efficient removal of bacteria and matrix
- Trilon M + Subtilisin: no additional effect compared to Trilon M
- Trilon M + Lutensol XL 60: additional effect with removal of bacteria compared to Trilon M
- Trilon M + Subtilisin + Lutensol XL 60: further enhanced removal of bacteria and matrix
Conclusion

- It was shown, that suitable nonionic surfactants for membrane cleaning do exist
- This rebuts the general assumption of their inapplicability
- Nonionic surfactants can be used, when
  - the HLB is in a range of 10 to 13
  - the fatty alcohol is branched
  - or selected extended surfactants are chosen
Conclusion

Compared with the current market standard LAS or alkylphenol ethoxylates these products have several advantages, they

- clean better and faster
- are compatible with enzymes
- are stable in alkaline and acidic media
- are low foaming
- are readily biodegradable and
- have a low aquatic toxicity

Preferred surfactants are Lutensol® XL 60 and Plurafac® LF 900
Thank you for your attention!