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Scaling up continuous mixing process of liquid laundry additives made up of self thickening surfactants solutions

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Liquid detergents and additives often own their microstructure and rheological properties to mixed surfactants micellar solutions. These systems are usually manufactured via continuous mixing process where all the ingredients are incorporated into an aqueous basemix by in line static and dynamic mixers. The scale up of these manufacturing processes is frequently not trivial and product rheology and microstructures often change when process conditions and production scale vary. Usually these systems are assimilated to emulsions, whose scale up criteria is far better understood. The primary goal of this work is to show by means of an example, how different and more complex can be the behaviour and dynamics of self thickening surfactants solution versus that of emulsions. For the liquid additive formulation we have studied, we have found that varying production rate, scale and order of addition we can either form stable products which reach their final rheology within few hours of rest or produce unstable solutions whose rheology reaches its final steady only after weeks or months from production. We have empirically identified and verified at various scales a scale up parameter capable of describing both short term and long term dynamics of these products. Possible interpretation of these results are discussed with the aim of identifying a more general scale up approach for in line mixing of self thickening surfactant systems.

1. Introduction

Diluted liquid detergents and additives are typically formulated using mixed surfactants system (ionic and non ionic). These products are usually formulated to be macroscopically homogeneous microemulsions by addition of solvents and hydrotropes. The usage of different surfactants leads to the formation of mixed micelles with a high effective average critical packing parameter thus leading to the formation of self thickening systems made up of worm like micelles (Laughlin, 1994).

Worm like micelles are usually linear viscoelastic fluids which own their elasticity to the entanglement of micellar chains, while their relaxation time is due to fastest stress relaxation process between chain reptation and micelles breakage. When micelles breakage is the fastest relaxation time, the system behaves as a pure single relaxation time Maxwell linear viscoelastic fluid, while when stress relaxation is due to micellar chain reptation the system is polydisperse with a broad relaxation time spectra (Spenley, 1993)

Predicting rheological and other physical properties from detergent composition is difficult, being detergents multi-component complex mixtures, and the formulation of these products is usually done by empirical optimization techniques.

Liquid detergents are often produced via continuous processes where the incorporation of all the ingredients into the aqueous base is accomplished via static (e.g. Sulzer or Chemineer) or dynamic (e.g. rotor stator ex Ika or Bran & Luebbe) mixers. It is often difficult to predict from experiment made at bench scale or pilot plant the physical properties of products made at full manufacturing scale, as a matter of fact, there is no accepted general scale up theory of mixing for self thickening worm like surfactants solutions.

The current best approach within detergent industry is that of assimilating these detergent products to emulsions which are far better studied and understood. For emulsification, the accepted scale up parameters, are respectively constant capillary number in laminar flow (Grace, 1982) and constant Weber number or dissipated power per unit of volume in turbulent flow (Berkman, 1988). In both cases it is safely kept constant the average residence time.

The assimilation of micellar solutions to emulsion brings both theoretical and practical issues. From a theoretical standpoint, for emulsions the creation of surface area requires energy, while for surfactant solutions far above the critical micellar concentration the surface area is constant and just depends on surfactants concentration and layer density (Israelachvili 1991), while energy is required to bend surfactants layers to form a given micellar shape. From a practical standpoint, being the system self thickening it is not uncommon that the flow is turbulent due to low ingredients viscosity at the entrance of the mixer and it becomes viscous at the exit of the mixer or whenever the final viscosity is built up.

In this paper we experimentally analyse the scale up problem of a model liquid laundry additive with the objective of identifying a suitable scale up parameter and experimental results are discussed in order to identify a suitable model for micellar solution manufacturing which could lead to a better theoretical framework to scale up these systems.

2. Materials and methods

2.1 Materials

The liquid additive used in these experiments is based on a ternary surfactants system made up of a hydrophilic non ionic ethoxylated alcohol:

Marlipal 24 7 (ex Sasol): alkyl chain length C12 – C14, average Ethoxylation (EO) number 7 a hydrophobic ethoxylated alcohol:

Neodol 23 1.1 E (ex Shell): alkyl chain length C12 – C13, average EO number 1.1

and an anionic surfactant:

sodium dodecyl-benzene-sulphonic acid (HLAS)ex Procter & Gamble.

While full product composition is not disclosed for confidentiality reasons, all the other ingredients are low molecular weight water soluble molecules. In the next section this product is fully characterised from rheological standpoint.

2.2 Preparation of liquid additive

The liquid additive used in these experiments have been prepared first at bench scale in an agitated glass beaker with mechanical agitation adding all the ingredients one after the other, leaving surfactants as last ingredients. In order to exclude a manufacturing effect, the very same product was made with different beaker size (1 and 5 Lt), different impeller agitation (150 and 500 RPM) and with different mixing time after last ingredient addition (10 and 20 minutes). All products made in this way showed the very same rheological properties which remained constant in time up to several weeks ageing at 20 °C. The very same product was prepared via a continuous mixing process where all the ingredients were incorporated into the water main stream by means of a Kenics KM or Sulzer SMX static mixer. The order of addition was always the same and it was water, all soluble ingredients, then Marlipal 24 7, Neodol 23 1.1 E and HLAS as last ingredient. During the course of the experimental campaign, we changed static mixer type, diameter and flow rate as it will be illustrated in the next section.

2.3 Physical characterization

All the products produced in these experiments were characterised visually using a Zeiss Axiovert 40 optical microscopy to exclude the formation of birefringent liquid crystalline phases (Sein, 1993) and rheologically both in flow and oscillatory mode, using a cone and plate stress controlled AR 2000 rheometer ex TA instruments.
The batch made product is a shear thinning (Fig 1), linear viscoelastic fluid (Fig. 2) with multiple relaxation times.

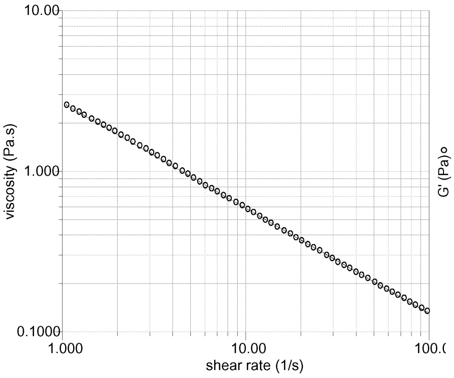

Fig 1: viscosity of batch product

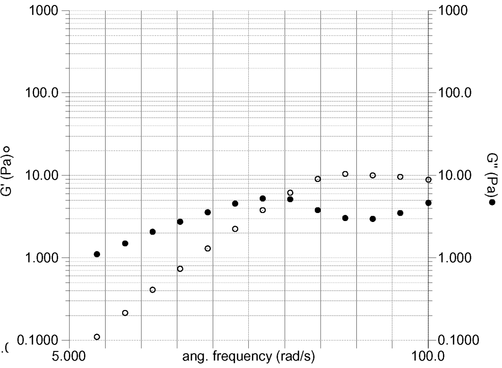

Fig. 2 viscoelastic spectra of batch product

3. Results and discussion

3.1 Experimental plan

In order to understand the right scale up criteria for continuous manufacturing process we produced this product at different flow rates and pipeline diameters using different static mixers as described in table 1

Table 1: Summary of experimental trials

Trial Number	Flow rate (m3/hr)	Pipe internal diameter (mm)	Mixer type	Residence time (sec)	Reynolds number
1	0.9	36	Sulzer SMX	1.13	64
2	1.3	36	Sulzer SMX	0.78	112
3	2	36	Sulzer SMX	0.51	223
4	1.3	25	Sulzer SMX	0.33	288
5	2.5	25	Kenics KM	0.33	543
6	2.5	25	Kenics KM	0.50	543
7	40	100	Sulzer SMX	0.75	2300

For each experiment, we calculated Reynolds number by using the product rheology of the standard batch made finished product fitted via equation 1 (using K =2000, n = 0.56) and using the viscosity at average static mixer shear rate:

$$\text{Average shear rate } = \frac{Q}{A \cdot d} \qquad (2)$$

Where Q is the flow rate, d is the static mixer diameter and A is the static mixer cross area. From the table above it is evident that the flow pattern is laminar to transition, but never fully turbulent and using the scale criteria valid for the emulsions the system should scale up with average shear rate.

Additionally, for each experiment we calculated the power dissipated per unit of volume by empirically measuring the pressure drop over the static mixer using the following formula:

$$\frac{Power}{Volume} = \frac{\Delta p}{L} \cdot \frac{Q}{A} [=] \frac{Kw}{m^3} \qquad (3)$$

Where Δp is the pressure drop and L is the static mixer. All the power per unit of volume data, obtained in this way are summarised in Table 2.

Table 2: summary of measured power per unit of volume

Trial Number	Power per unit of volume (P/V) (Kw/m^3)
1	3.0×10^0
2	1.0×10^1
3	3.5×10^1
4	1.3×10^2
5	1.5×10^2
6	1.5×10^2
7	2.2×10^2

3.2 Rheological characterization results

All the products produced as per the experimental plan above were characterised for flow rheology both freshly made and over ageing. Fig. 3 shows that the batch made products present a shear viscosity almost constant over ageing, all the products made via continuous process as mentioned above present viscosity variation over several days

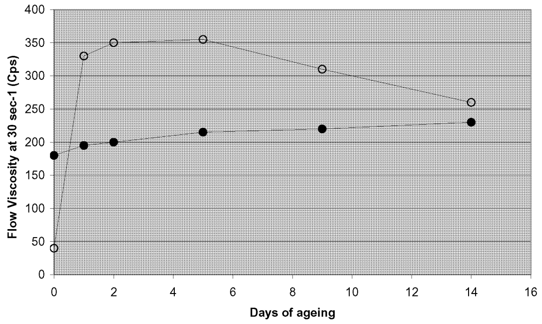

Fig. 3 viscosity variation versus time for both batch made (• solid dots) and in line made (Trial 3, O open dots) products.

Additionally, the batch made product shows always a constant shear thinning index of about 0.6, while product made in static mixer is Newtonian as made, highly shear thinning after 3 days (~ 0.3 shear index), then after 15 it shows a shear index (~ 0.6) comparable to that of batch made products. In Fig 4, we plot the viscosity at 30 sec-1, measured after 2 days, of static mixer made products versus the measured power per unit of volume. This graph shows that the rheology of this product made using static mixers, to a good extent even regardless of static mixer type and residence time through static mixer, scales up with calculated power per unit of volume

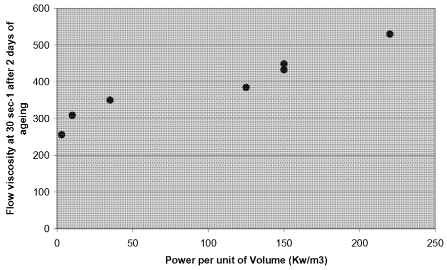

Fig. 4 flow viscosity at 30 sec-1 after 2 days ageing versus power per unit of volume

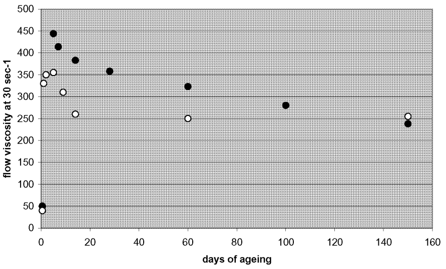

Fig. 5 flow viscosity over long term ageing versus a high P/V (trial 7, • solid dots) and a medium/low P/V (Trial 3, O open dots) products.

In Fig. 5, we plot the long term ageing of two producrt made with both an high and a medium to low power per unit of volume. The results indicate that the time to reach an equilbrium viscosity depends on power per unit of volume. While the equilibrium viscosity of the product seems to be independent from this.

3.3 Results interpretation and discussion

The experimental data presented so far show that micellar solution can present a very different behaviour from that of emulsion and a quite complex dynamics. While mixing des not alter the long term equilibrium rheology and microstructure, it does affect the short term product rheology. We believe this behaviour can be qualitatively explained if we compare the micellization to process to a set of competitive chemical reactions (Patist, 2002) . Mixed micelles are formed when surfactant monomers of different type react together; the availability of surfactant monomers determines the mixed micelle composition and hence rheology. While at equilibrium the mixed micelles composition is set by mass balance and thermodynamics, during a fast micellization process, like the one happening in a static mixer, the availability in solution of different monomers is determined by the dissolution rate and hence by their solubility. Neodol 23 1.1 E monomers, (nearly insoluble in water) are slowly released and thus they micellize on their own rather than in a mixed micelle. Over ageing, mixed micelles composition equilibrates reaching the steady state which is process independent. In order to re-equilibrate, surfactant monomers must re-dissolve in solution and re-micellize, this is a slow process for very low solubility surfactants like the Neodol 23 1.1 E.

4. Conclusion

The primary goal of this paper was to show by means of an example the scale up problem of in line mixing of self thickening surfactants solution. We have shown that fast in line mixing can initially generate an out of equilibrium mixed micelles system, which reach its final steady state within weeks or months. We have postulated a qualitative model for this behaviour and proposed a scale up.

5. References

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