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Surfactants as Rheology Modifiers – Cationic Thickeners

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abstract

Amine derived thickening agents can be used to impart viscosity and favorable rheological properties to cleaning formulations. The viscosity is a result of complex and dynamic micelles formation that can be extended to rods and entangled worm-like structures. Cationic surfactants are versatile functioning ingredients that have been used in many challenging formulations where extreme pH or oxidative mediums are desired. In addition to thickening, surfactants bring other benefits such as degreasing efficiency, foam control, oil and perfume solubilization, particle dispersion, and corrosion inhibition.

Introduction

Household cleaners are not only thickened for technical and safety reasons, physical appearance plays a very important role for the end users. For example, a viscous product is perceived as more concentrated and therefore more effective than a lower viscosity product. Higher viscosity ensures better adhesion, uniform coverage and a better rinse-off. A uniformly built 'curtain' increases the contact time between the cleaner and the contaminants present on the surface which is especially important for inclined and/or vertical surfaces such as toilet bowls, tile walls, etc. However, there are obvious upper limits to the viscosity of a cleaner. The cleaning solution must be thin enough to squeeze out of a bottle or flow through a dosage control dispenser. At the same time, viscosity can be used to minimize accidental product releases in the form of splashing and leaking. Finally, thickening provides colloidal stability which can be used to stabilize active components in the formulation and increase shelf life. Clearly, imparting viscosity and rheological behavior into a detergent formulation enables formulators to bring specific properties and appearance into new cleaning products and augment their value.

There are many different thickening agents available for consumer products and in all cases there is a direct and strong

link between the molecular microstructure and the macroscopic flow behavior of the formulation.

In general terms, a rheologically complex system at rest can have randomly oriented molecular assemblies or structures corresponding to a minimum energy state. When low level of shear stress is applied, the system will resist deformation and typically exhibit a high and relatively constant viscosity. As the level of shear stress is gradually increased, the structural units are forced to respond to the applied stress and begin to deform. They react either by aligning themselves in the direction of the flow (e.g. polymer chains), or by deforming to orient along the streamlines (e.g. emulsion drops), or by separating into smaller units (e.g. micellar structures). Similarly, entangled structures may become disentangled and may even fully straighten. Eventually, as more and more shear stress is applied fewer changes are possible in the structure or orientation and the system displays a lower and constant viscosity. This article reviews how amine based surfactants, such as fatty amine ethoxylates, quaternary ammonium salts and fatty amine N-oxides, can be used to thicken aqueous systems and different factors affecting their rheological profile. Examples of their applicability in cleaning formulations across the entire pH range will also be presented.



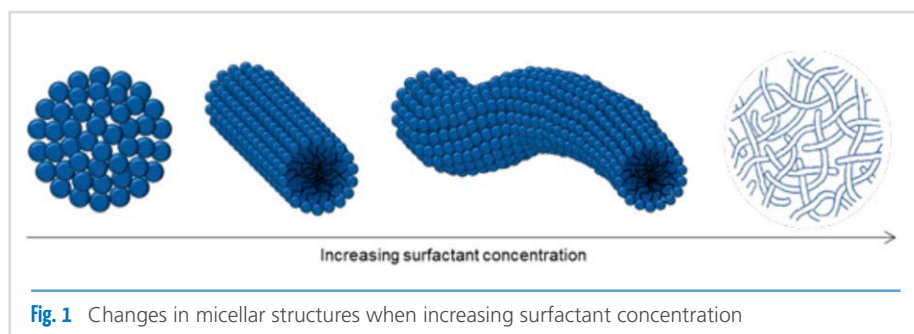


Fig. 1 Changes in micellar structures when increasing surfactant concentration

bicity that influence how it will pack into dynamic micelle structures. The tendency to grow larger and elongated micelles increases strongly with hydrophobicity. **Fig. 2** shows the rheological behavior of acidic formulations thickened with coco, oleyl and tallow based ethoxylated amines. The hydrophobicity increases with the length of the carbon chain and decreases with

Micellar Growth for Cationic Surfactants

As it is well known, surfactants are amphiphilic molecules, containing both hydrophilic and hydrophobic parts. The unfavorable interaction between water and the apolar part of surfactant molecules drives their self-assembly. At a certain surfactant concentration in an aqueous solution, the Critical Micellar Concentration (CMC) is reached and surfactant molecules aggregate. Those aggregates, called micelles, display a rich polymorphism that provides very different physicochemical properties in the bulk solution. The shape of the micellar structure formed depends mainly on the surfactant structure. For most common surfactants, the first-formed micelles are spherical in shape, that grow in size as the surfactant concentration increases. At some point, further increase in surfactant concentration will promote the formation of cylindrical micelles (**Fig. 1**). These long semi-flexible worm-like structures form, by entanglements, a three dimensional dynamic network which is the source of the drastic increase in both viscosity and elasticity observed when rising concentration of certain surfactant solutions.

Surfactant concentration is not the only factor playing a role in micelle growth. Subtle changes in the molecular structure of the surfactant (alkyl chain length, branching, unsaturation as well as counter ion) and/or the physicochemical conditions (temperature and co-solutes) will affect the size and shape of the microstructures formed.

One of the main factors to consider is the overall geometry of the surfactant and its hydropho-

phobicity. The products compared in **Fig. 2**, indicate that thickening increases in the order: coco < oleyl < tallow, as expected. A clear difference in their rheology profile is also observed, especially at lower shear rates confirming that longer and more saturated alkyl chains build longer micelles and therefore thicker products. (**Tab. 1**)

The most well-known and studied wormlike micelles systems are cationic surfactants with a long aliphatic chain, for which micellar growth takes place at relatively high concentration or in the presence of desolubilizing additives. Desolubilizers have the effect of screening repulsions between the exposed surfactant head groups and thus shift the vis-

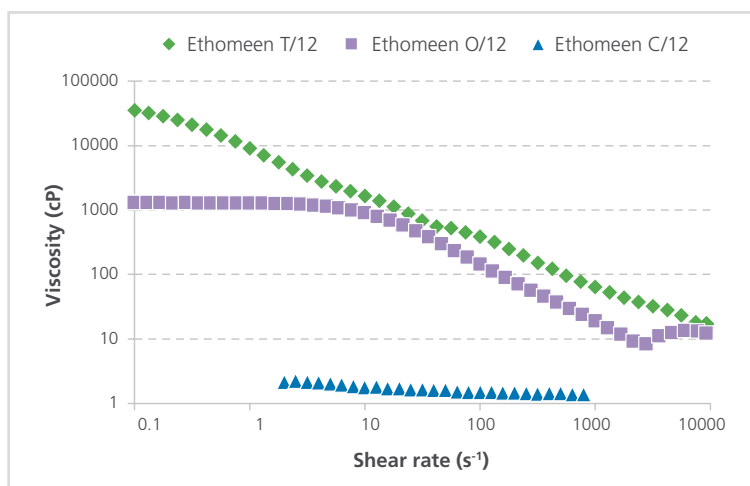


Fig. 2 Rheology profiles of three acidic formulations containing 2% ethoxylated amine with different hydrophobicity (coco < oleyl < tallow), 3.7% hydrochloric acid and balanced with water

Surfactant	Raw material	Main carbon chain length	Fatty acid composition (Percentage of total fatty acids)		
			Saturated	Monounsaturated	Polyunsaturated
Ethomeen T/12	Tallow	C16-C18	52	44	4
Ethomeen O/12	Oleyl	C18	14	77	9
Ethomeen C/12	Coco	C12-C14	92	6	2

Tab. 1 Comparative table of the different properties affecting the hydrophobicity of fatty amines ethoxylates tested

cosity increase towards lower concentrations (Fig. 3). As a consequence, head to head repulsion forces in the micelles are minimized, the effective head group for each surfactant is reduced which promotes packing of the hydrophobic tail and micellar growth.

In addition to micellar shape and size, the rheology profile of the final formulations also depends on the physicochemical

properties of the whole system. Organic salts such as sodium xylene sulfonate (SXS), sodium cumene sulfonate (SCS), soaps, as well as electrolytes act as desolubilizers. On the other hand, nonionic surfactants such as fatty alcohol ethoxylates, e.g. Berol 175 (C12-16 + 7.5 EO), have a solubilizing effect. Desolubilizing and solubilizing agents can be used to fine tune the viscosity profile, either to thicken the formula or to thin it to avoid elastic properties where the product does not flow and has no practical use.

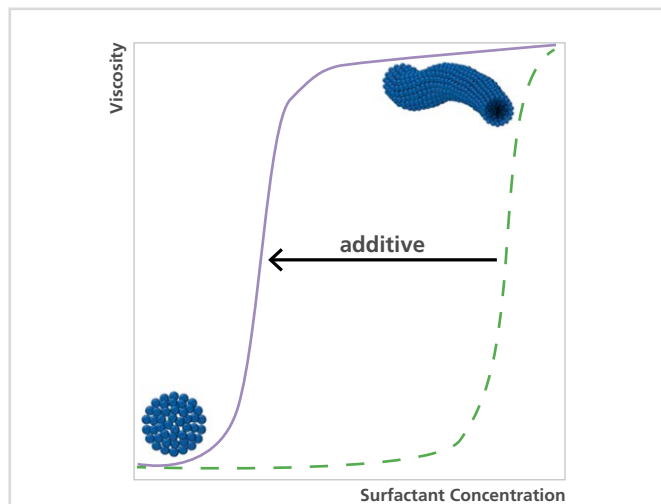


Fig. 3 Micelles formation and viscosity changes with desolubilizing additives

Classes of Thickening Agents

The product portfolio of AkzoNobel Surface Chemistry includes several classes of amine derived thickening agents:

Ethoxylated Amines

- Ethomeen C/12 (Bis(2-hydroxyethyl) coco alkylamine; 100 % active)
- Ethomeen O/12 (Bis(2-hydroxyethyl) oleyl amine; 100 % active)
- Ethomeen T/12 (Bis(2-hydroxyethyl) tallow alkylamine; 100 % active)
- Ethomeen HT/12 (Bis(2-hydroxyethyl) hydrogenated tallow alkylamine; 100 % active)

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- Arquad 16-50 (hexadecyl trimethyl ammonium chloride; 50 % active)
- Arquad T-50 (tallow trimethyl ammonium chloride; 50 % active)

Amine Oxides

- Aromox 14D-W970 (tetradecyl dimethyl amine oxide; 25 % active)
- Aromox T/12 (tallow bis(2-hydroxyethyl) amine oxide; 50 % active)

Cationic thickeners can be used to modify the viscosity of formulations at any pH (Fig. 4) and even in extreme conditions such as highly acidic and alkaline formulations with or without oxidative agents. As examples, Arquad 16-29 and Arquad 16-50 are stable in hydrogen peroxide while Aromox 14D-W970 is stable in high alkaline and hypochlorite based formulations. Besides thickening, surfactants bring additional benefits such as degreasing efficiency, foam control, oil and perfume solubilization, particle dispersion, and corrosion inhibition.

Thickening Formulations

Our broad portfolio of cationic surfactants provides thickening solutions for a wide range of applications. Their ability to control the rheological behaviour in extreme acidic, alkaline or oxidative mediums needs to be highlighted. **Tab. 2-4** present different formulations for those conditions, while **Tab. 5** presents the effect of adding Berol 175 to different formulations.

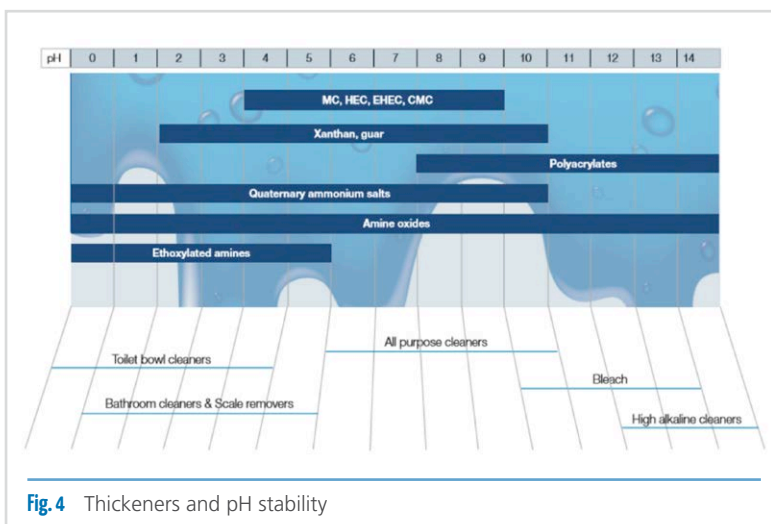


Fig. 4 Thickeners and pH stability

Ingredients	% w/w (as is)						
Hydrochloric acid 37 %	10	10	10	10	25.6	25.6	25.6
Ethomeen O/12	1.5	1.5	-	-	3	-	-
Ethomeen T/12	-	-	-	2	-	1	1.5
Aromox T/12	-	-	1.5	-	-	-	-
Arquad T-50	-	1.5	1.5	-	-	1	1
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity (cP) Brookfield sp 3 at 30 RPM and RT	420	480	320	932	630	700	1500

Tab.2 Thickening hydrochloric acid formulations with cationic surfactants

Ingredients	% w/w (as is)										
Citric acid 100 %	5	5	-	-	-	-	-	-	-	-	-
Phosphoric acid 85 %	-	-	58.8	58.8	3.5	3.5	-	-	-	-	-
Oxalic acid	-	-	-	-	-	-	5	10	10	-	-
Sulfamic acid 100 %	-	-	-	-	-	-	-	-	-	10	5
Ethomeen O/12	1	-	-	2	2	-	2	2	-	-	-
Ethomeen T/12	-	-	2	-	-	-	-	-	1.5	2	1.5
Arquad T-50	-	2	-	-	-	2	-	-	-	-	-
SXS	1	1.5	1.5	1.5	1	1	1	1	1	1	1
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity (cP) Brookfield sp 3 at 30 RPM and RT	400	290	1250	1820	320	510	1290	470	560	790	550

Tab.3 Thickening organic acid formulations with cationic surfactants

Procedure

The typical procedure to use cationic surfactant thickeners in formulations:

1. Prepare the acidic, alkaline or oxidative medium by dissolving it in water.
2. Prepare a solution of the cationic thickener and the fragrance in water.
3. Add together the pre-diluted solutions from steps 1 and 2.
4. Add desolubilizer to increase the viscosity.
5. Add solubilizer to fine tune the rheological behaviour of the system.

Ingredients	% w/w (as is)						
	30	10	5	5	-	-	0.5
NaOH 100 %	30	10	5	5	-	-	0.5
Hydrogen peroxide 30 %	-	-	-	-	16.7	16.7	-
Sodium hypochlorite 15 %	-	-	-	-	-	-	70
Citric acid 100 %	-	-	-	-	3	-	-
Sulfamic acid 100 %	-	-	-	-	-	3	-
Aromox 14D-W970	-	3	-	-	-	-	4
Aromox T/12	3	-	1	-	-	-	-
Arquad T-50	-	-	-	2.5	-	3.5	-
Arquad 16-29	-	-	-	-	3.5	-	-
Ampholak YCE	0.75	-	-	-	-	-	-
SXS	-	1.5	-	1	1.5	1.5	-
Sodium carbonate	-	-	-	-	-	-	4
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity (cP) Brookfield sp 3 at 30 RPM and RT	2500	180	350	580	670	400	600

Tab.4 Thickening alkaline and bleach based formulations with cationic surfactants

Ingredients	% w/w (as is)			
	10	10	-	-
Hydrochloric acid 37 %	10	10	-	-
Oxalic acid 100 %	-	-	5	5
Ethomeen O/12	-	-	2	2
Ethomeen T/12	2	2	-	-
SXS	-	-	1	1
Berol 175	-	1	-	0.3
Water	q.s.	q.s.	q.s.	q.s.
Viscosity (cP) Brookfield sp 3 at 30 RPM and RT	1960	300	1290	580

Tab.5 Berol 175 as rheology modifier in formulations with cationic thickeners

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