

THICKENING OF FOAMING COSMETIC FORMULATIONS

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Abstract

Enhancing the viscosity of a foaming cosmetic formulation has both marketing and technical reasons. A rich appearance will be correlated by end users with high concentration and value for money. Thickening also has an advantage in applying the product: a thin shampoo would run off the hands easily. In formulation development and optimization, a thickened formulation can also allow keeping heterogeneous solutions in a stable equilibrium.

This paper gives an overview of the different ways of incorporating viscosity in a surfactant formulation including an explanation of the mechanisms involved. It summarizes the different types of raw materials available to formulators illustrating their advantages and drawbacks. The second part gives an overview of typical frame formulations of commercially available shampoos and shower gels. Finally, this paper presents an up-to-date list of most widely used alternatives to diethanolamine based surfactants whilst showing their performance. The comparative study illustrates the superiority of one of the selected alternatives from point of view of workability and similar viscosity build-up performance in a formulation as Cocamide DEA.

Introduction

Enhancing the viscosity of a foaming cosmetic formulation has both marketing and technical reasons. A rich appearance will be correlated by end users with high concentration and so gives them the impression that they get value for money. Thickening also has an advantage in applying the product: low viscous liquids are difficult to apply to hair and skin; more viscous products will not run off the hands too easily. In formulation development and optimization, a thickened formulation can allow keeping heterogeneous solutions in a stable equilibrium and simplifies the design of suitable packaging.

In a first part, this paper gives an overview of the possible ways of incorporating viscosity in a cosmetic surfactant solution including an explanation of the different mechanisms involved. The information is reviewed from a formulator's point of view. The second part gives an overview of typical frame formulations of commercially available shampoos and shower gels. Finally, this paper presents an up-to-date list of most widely used alternatives to diethanolamine based surfactants whilst showing their performance. This presentation does not address alkanolamide safety, but focuses rather on formulating with alternatives that stay within the cost/performance parameters of alkanolamides.

1. Solutions for thickening of cosmetic detergent solutions

Considering that the thickening of cosmetic detergent solutions refers to increase of viscosity of shampoos, shower gels and bath foams, a wide range of thickening additives of different chemical nature is available to formulators. The expression 'thickening agent' is often immediately related to water dispersible polymers that are used to adjust the viscosity of products to make them easy-to-use as well as to maintain the product stability. These raw materials can eventually be classified into natural polymers, semi-synthetic polymers and synthetic polymers. In the past, natural polymers formed the mainstream led by natural gums such as tragacanth, guar and carrageenan. Problems with securing stable supplies

coupled with problems such as variation in viscosity and microbial contamination led to a change to synthetic and semi-synthetic substitutes. Currently, synthetic thickening agents are in the majority.

Xanthan Gum is an example of a still widely used natural gum. It is an acidic polysaccharide composed of D-glucose, D-mannose and D-glucuronic acid. It has good usage characteristics especially thanks to low temperature dependence and stability over a wide pH range.

Considering semi-synthetic polymers, important products, in terms of the numbers of foaming cosmetic formulations containing them, are Hydroxyethylcellulose and Hydroxypropylcellulose. These cellulose derivatives are stable at acid pH, compatible with electrolytes and fairly resistant to bacteriological contamination. The choice between one and the other is based upon compatibility with the detergents, clarity and viscosity required. They are widely used in combination with mild sulfosuccinates and sarcosinates.

Polymers of acrylic acid and vinyl pyrrolidone as well as polymers of ethylene oxide and propylene oxide can be designated by the term synthetic polymers. In the past, typical Carbomer have been widely used. It is now being replaced by materials such as Acrylates/C10-30 Alkyl Acrylate Crosspolymer. On neutralization of the acidic dispersion of Carbomer, thickening occurs depending on the amount of polymer used. Polyvinyl Pyrrolidone (PVP) dissolves easily in water to form a viscous liquid. It is used in hair care products due to its film-forming properties and close affinity for hair, as well as in shampoos to stabilize the lather and give luster to hair.

Polymers of ethylene oxide are well known under the form of a large range of polyethylene glycol derivatives. So called EO/PO block copolymers are better known under the INCI name Poloxamer. Some of them are also useful viscosity controlling agents. PEG-150 Distearate also called PEG-6000 Distearate is a last example of a polymeric high MW surfactant with a hydrophobic/hydrophilic/hydrophobic structure.

The viscosity effect of such polymers in dilute aqueous surfactant solution results from the build-up of a three dimensional hydrated network in the water phase, in which surfactant micelles are trapped. Synergistic interactions between micelles and polymers further increase the viscosity. Similarly this mechanism is valid for synthetic copolymers and chemically modified natural polymers which are well known as thickening agents. Polymeric substances like natural gums and cellulose derivatives will also cause viscosity building by entangling of the polymer backbone. Another obvious mechanism influencing viscosity build-up of a formulation is hydrogen bonding; a higher degree of hydrogen bonding will cause a formulation having a higher viscosity as more complex aggregates on molecular scale will result in a more rigid structure. Before any natural or synthetic polymer is used, it should be considered that it may alter the feel of the produced foam, act as a foam stabilizer, form a film on the hair or the skin or alter the products' cloud points. It may also require a more effective preservative system.

In many cases, as will be shown in paragraph below, foaming cosmetic formulations are mainly based on alkyl ether sulphates mixed with a mild co-surfactant (betaines or amphoteric), and the viscosity is achieved by addition of salt and/or fatty acid alkanolamides or nonionic alternatives to Cocamide DEA (for instance low ethoxylated fatty alcohol) and not by the use of previously described raw materials.

Alternatives to Cocamide DEA will be discussed more in detail in last paragraph of this paper. As inorganic salts are often present as byproduct in raw materials themselves, nearly all cosmetic detergent formulations start with some amount of electrolyte. Fatty alcohol sulfates and fatty alcohol ether sulfates solutions are easily thickened by additional amounts of ammonium chloride, sodium chloride or sodium sulfate. Viscosity is of course dependant on the amount of electrolyte. In practice, electrolyte additions of between 0.1 and 3% are usually made, depending upon the formulation composition, concentration and viscosity required. Obtained viscosity is sensitive to temperature. Foam needs to be increased with foam stabilizers/boosters such as Cocamide DEA or its proposed alternatives that give a pronounced thickening effect in combination with electrolyte.

In most formulations, micelle interaction and intermolecular association will be the mechanism controlling viscosity. When a secondary surfactant such as an alkanolamide or a low ethoxylated fatty alcohol interacts with a primary surfactant such as an alkyl ether sulfate this results in a re-organisation on the molecular level. The primary surfactant, normally organised in solution in isometric spherical micelles, will undergo a structural change that can result in a transformation to anisometric rod- or disc-like micelles and even to dynamic networks. The consequence of this type of re-organizations is a macroscopic

observed increase in viscosity. The effect of inorganic salts is to be understood in the same context. An electrolyte like sodium chloride will increase the ionic strength of the bulk phase resulting in the formation of larger micelles and thus having a positive influence on the viscosity as long as the ionic strength is not too important.

Finally, the viscosity of a formulation can strongly be influenced by its pH. In general, viscosity will increase upon decrease of pH.

2. Composition of commercial foaming cosmetic formulations

In the past, in most formulas alkanolamides (in particular Cocamide DEA) were combined with an anionic surfactant to build viscosity, boost and stabilize foam, stabilize the finished product and lower costs. Over the past decades, the development of daily use products with high skin compatibility caused an increased demand for very mild surfactants requiring improved efficacy of preferably diethanolamine free thickening agents. Historically, fatty acid alkanolamides were the principal secondary surfactants followed by amine oxides but currently amphoteric including Cocamidopropyl Betaine, Sodium Cocoamphoacetate and Disodium Cocoamphodiacetate are used on account of their excellent reduction in irritation. As shower gels have much in common with simple shampoo formulations and, unlike bath products, they are applied directly to the skin, both type of products have been considered for studying the nowadays most widely used frame formulations in the area of foaming cosmetics formulations.

Looking at products widely available in supermarkets on the Belgian market, following observations can be made from point of view of composition of standard shower products (considering their four main ingredients excluding water and humectant):

- A same primary surfactant is used in all products: Sodium Laureth Sulfate.
- The most important high level secondary surfactants are Cocamidopropyl Betaine (found in 70% of the products) and Cocamide DEA (15% of the products). Other high level secondary surfactants are Coco-Glucoside and Disodium Laureth Sulfosuccinate.
- The lower level secondary surfactants when they are used are mainly Coco-Glucoside (30% of the products) and Disodium Cocoamphodiacetate (25%). Other lower level secondary surfactants or thickening agents are Cocamidopropyl Betaine, Disodium Cocoyl Glutamate, Decyl Glucoside, Lauryl Glucoside, Cocamide MEA, PEG-200 Hydrogenated Glyceryl Palmate and Sodium Lauryl Sulfate.
- Sodium Chloride can be found in the top four ingredients in 40% of the cases.

As far as shampoos are concerned, following conclusions can be drawn:

- Sodium Laureth Sulfate is used as primary surfactant in more than 90% of the cases. Two alternatives are an amphoteric like Cocamidopropyl Betaine and a nonionic like Polysorbate-80.
- The most important high level secondary surfactants are by far Cocamidopropyl Betaine (found in 45% of the products) and Disodium Cocoamphodiacetate (in about 30% of the references). Other high level secondary surfactants but with much lower incidence are Sodium Cocoamphoacetate, Cocamide DEA and Sodium Laureth Sulfate (when it is not used as primary surfactant).
- The lower level secondary surfactants, when they are used, are much more diversified than for the shower products. The most common ingredient is still Cocamidopropyl Betaine in 10% of the formulations. Other lower level secondary surfactants or thickening agents include Disodium Ricinoleamido MEA-Sulfosuccinate, Disodium Laureth Sulfosuccinate, Sodium Laureth-11 Carboxylate, Lauryl Glucoside, Cocamide MIPA, PEG-200 Hydrogenated Glyceryl Palmate, Laureth-2 and Laureth-4.
- Sodium Chloride can be found in the top four ingredients in 50% of the cases.

It may be concluded that commercial products are generally still prepared using blends of anionic and amphoteric or combinations of anionic, amphoteric and nonionic surfactants to impart mildness to skin whilst keeping a characteristic creamy foam. Inorganic salt and so called Cocamide DEA alternatives (thickening surfactants) as shown in table 1 are used for further optimization of the formulations.

Ingredients	Shower gel	Shampoo
Main component	Water	Water
Primary surfactant	Sodium Laureth Sulfate	Sodium Laureth Sulfate
Secondary surfactants	Cocamidopropyl Betaine	Cocamidopropyl Betaine or Disodium Cocoamphodiacetate
Additional surfactants	Coco-glucoside or Disodium Cocoamphodiacetate	Cocamidopropyl Betaine
Electrolyte	Sodium Chloride	Sodium Chloride
Thickening surfactants	PEG-200 Hydrogenated Glyceryl Palmate Cocamide MEA	PEG-200 Hydrogenated Glyceryl Palmate Cocamide MIPA Laureth-2 Laureth-4

Table 1: Frame recipes for shower gel and daily shampoo

Numerous Cocamide DEA alternatives are offered to the cosmetic and detergent industry. But, there is still no known product that can directly replace Cocamide DEA. Even Cocamidopropyl Betaine cannot easily be used as a 'plug-in' for Cocamide DEA. By adjusting Sodium Chloride and surfactant ratios, however, the formulating chemist can try to duplicate the properties of an anionic/Cocamide DEA formula. Raw materials answering the traditional name of 'thickeners' as described at the beginning of this paper are not widely used in cosmetic foaming products unless a true formulation stability problem has to be solved. This is most probably the reason that Xanthan Gum and Acrylates/C10-30 Alkyl Acrylate Crosspolymer are formulated into exfoliating body washes containing scrub agents.

3. Cocamide DEA and its alternatives

As mentioned earlier, this presentation does not address alkanolamide safety, but focuses rather on formulating with alternatives that stay within the cost/performance parameters of alkanolamides. As well known, fatty acid alkanolamides like Cocamide DEA boost the foam produced by anionic surfactants and stabilize it: they thicken the foam and prevent it from collapsing too soon. They also increase the viscosity of a formulation in combination with electrolyte. Table 2 gives a selection of widely promoted alternatives to Cocamide DEA.

INCI names of Cocamide DEA alternatives	Several suppliers
Cocamide MEA	X
Cocamide MIPA	X
Laureth-x (with x = 2, 3 or 4)	X
Cocamide MIPA (and) Laureth-x	X
PEG-200 Hydrogenated Glyceryl Palmate (and) PEG-7 Glyceryl Cocoate	X
PEG-4 Rapeseedamide	
PPG-2 Hydroxyethyl Cocamide	
Polyglyceryl-3 Caprate	
Glycereth-2 Cocoate	
C12-13 Alkyl Lactate	
Cocamidopropyl Betainamide MEA Chloride	

Table 2: Proposed alternatives to Cocamide DEA

Based on our study of composition of commercial shower gels and shampoos, considering feedback of cosmetic manufacturers and selecting the ingredients that are most beneficial to viscosity build-up of cosmetic surfactants solutions whilst keeping foam stabilization properties, following raw materials have been selected for comparison of their performance against Cocamide DEA in basic surfactant solutions:

- PEG-200 Hydrogenated Glyceryl Palmate (and) PEG-7 Glyceryl Cocoate (from several suppliers)
- Cocamide MIPA (and) Laureth-x (from several suppliers)
- PEG-4 Rapeseedamide.

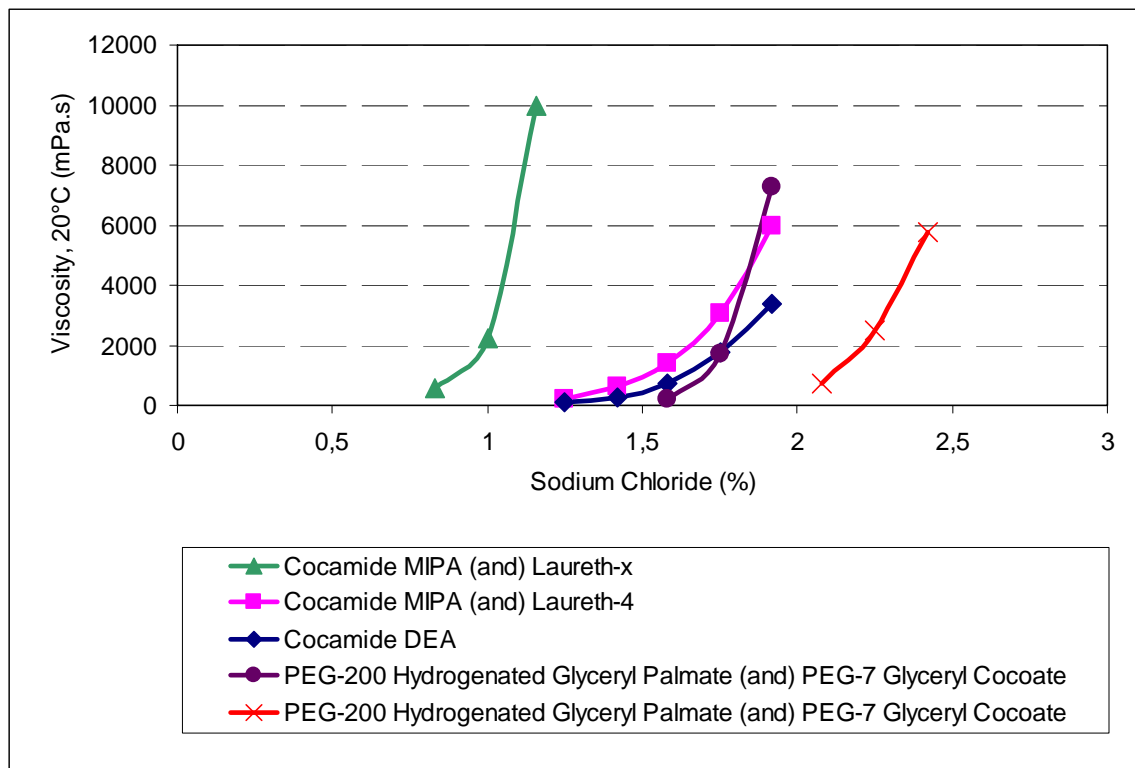
Although Cocamide MEA appears quite often in commercial references, it has not been selected due to its solid form.

The efficiency from point of view of thickening of a Sodium Laureth Sulfate solution of the selected alternatives to Cocamide DEA is shown in graph 1.

Ingredients	Amount (%w/w)
Water	to 100
Sodium Laureth Sulfate, 28%	45
Citric Acid	to pH 5.8
Thickening surfactant	3
Sodium Chloride	0.8 to 2.5

Table 3: Formulation details

All viscosities are measured at 20°C with a Brookfield RVT, using spindle 3, at 4 or 20 rpm, and are expressed in mPa.s.



Graph 1: Viscosity variation in function of amount of Sodium Chloride

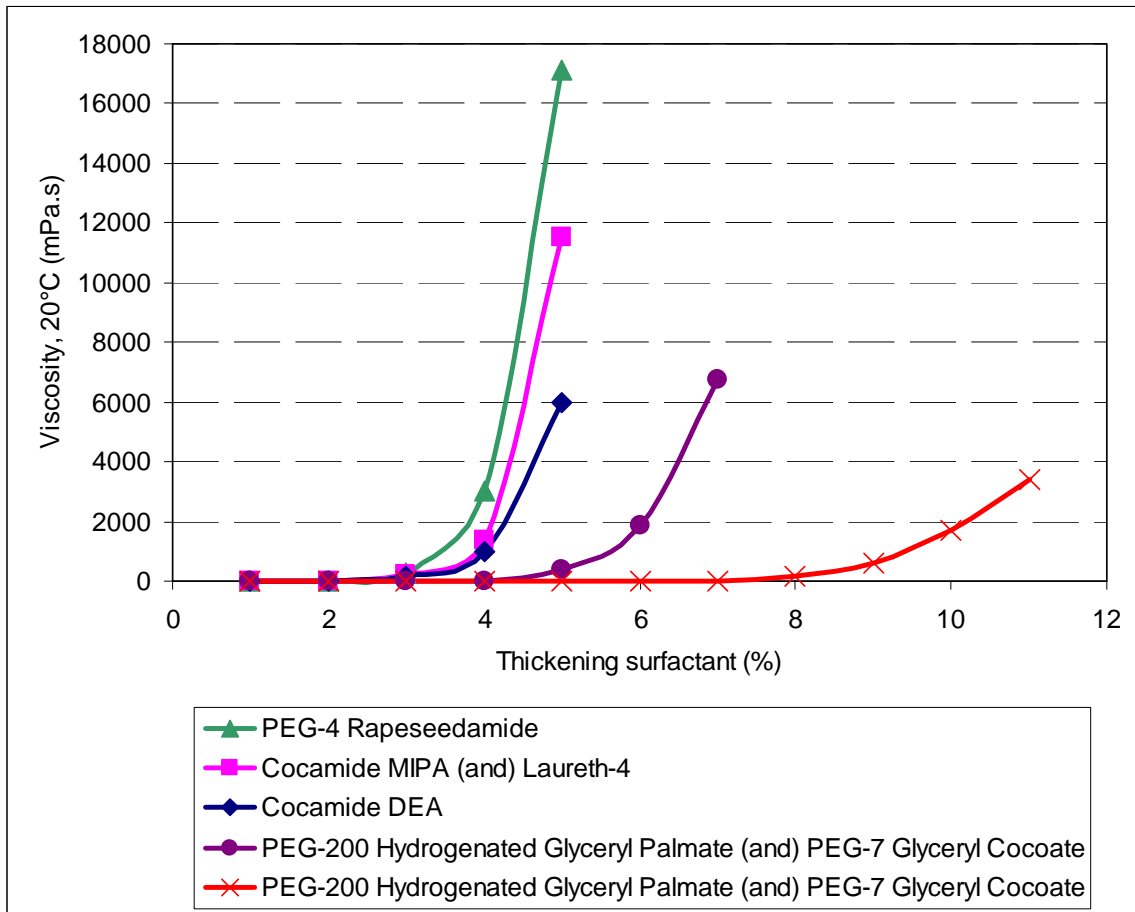
At high dosage level of thickening surfactant (3%), alternatives can be found that show close but not similar salt thickening response curves compared to Cocamide DEA. An important remark is that some raw materials with same INCI name show totally different behavior upon addition of the electrolyte solution.

Review of their performance the other way round, addition of thickening surfactant whilst keeping the amount of Sodium Chloride constant, is shown in graph 2.

Ingredients	Amount (%w/w)
Water	to 100
Sodium Laureth Sulfate, 28%	45

Citric Acid	to pH 5.8
Sodium Chloride	1.25
Thickening surfactant	1 to 11

Table 4: Formulation details



Graph 2: Viscosity variation in function of amount of thickening surfactant

Results observed in the first series of tests are confirmed. None of the tested surfactants shows exactly the same thickening performance as Cocamide DEA but some of them get close to the reference in the two series of tests: addition of a salt solution and addition of a thickening surfactant.

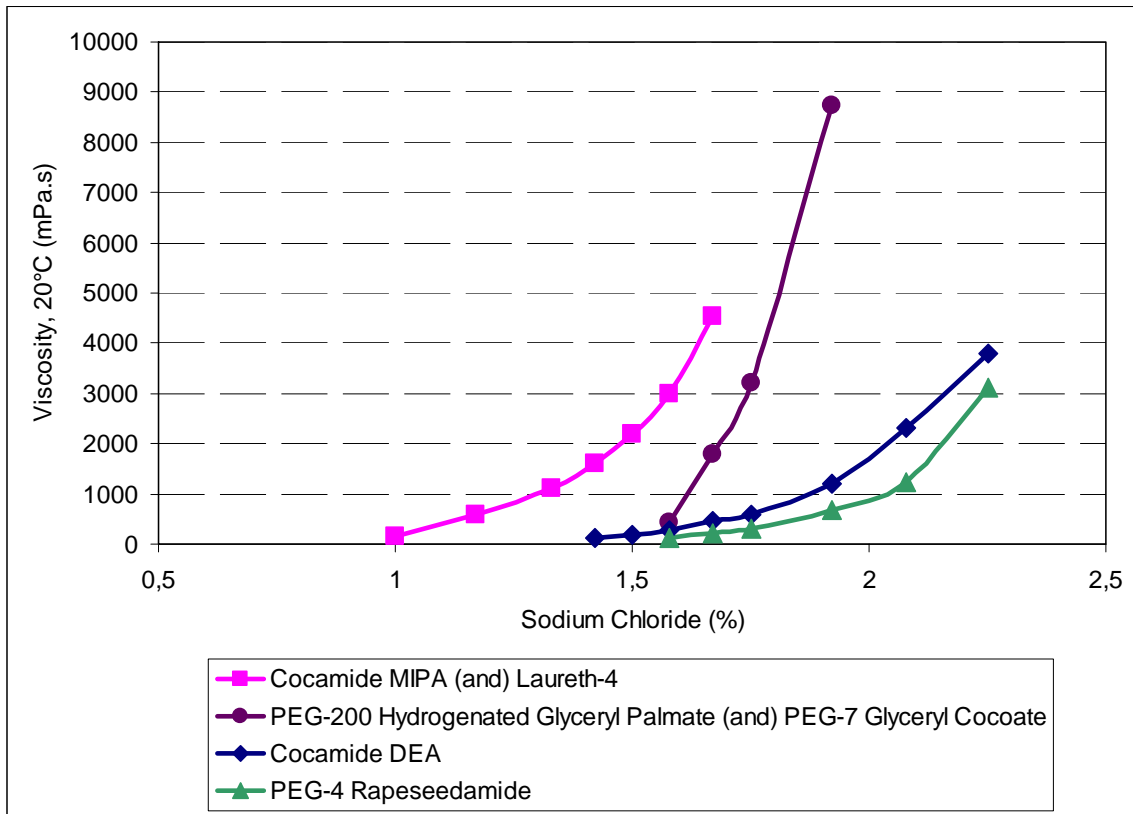
Fine-tuning of the amount of thickening surfactant in a formulation will be more difficult using PEG-4 Rapeseedamide (due its extremely quick viscosity increase) than with the product based on Cocamide MIPA and Laureth-4.

In further tests, the PEG-200 Hydrogenated Glyceryl Palmate (and) PEG-7 Glyceryl Cocoate product that shows the worse thickening properties will not be considered anymore.

Graph 3 shows the performance of the thickening surfactants when their respective activity is taken into account.

Ingredients	Amount (%w/w)
Water	to 100
Sodium Laureth Sulfate, 28%	45
Citric Acid	to pH 5.8
Thickening surfactant (activity)	2
Sodium Chloride	0.8 to 2.5

Table 5: Formulation details



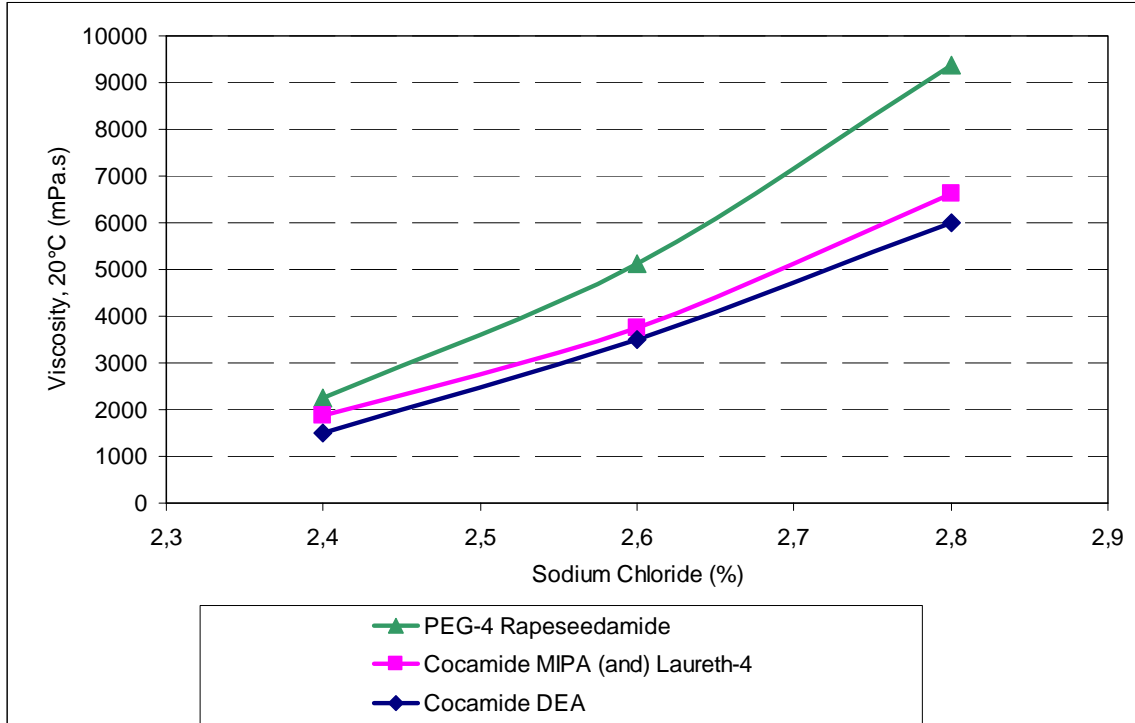
Graph 3: Viscosity variation in function of amount of Sodium Chloride

The blend of PEG-200 Hydrogenated Glyceryl Palmate and PEG-7 Glyceryl Cocoate shows quite important viscosity variations upon small differences in amount of Sodium Chloride. This is rather seen as a disadvantage compared to the other alternatives considering that in practice electrolyte levels in cosmetic raw materials themselves can slightly vary from batch to batch. From that point of view, PEG-4 Rapeseedamide and the blend of Cocamide MIPA and low ethoxylated fatty alcohol show more interesting performance.

In following series of tests (graph 4), the two remaining candidates are compared against Cocamide DEA at constant dosage level (2% instead of 3% in graph 1) and upon addition of a Sodium Chloride solution.

Ingredients	Amount (%w/w)
Water	to 100
Sodium Laureth Sulfate, 28%	45
Citric Acid	to pH 6.0
Thickening surfactant	2
Sodium Chloride	2.4 to 2.8

Table 6: Formulation details



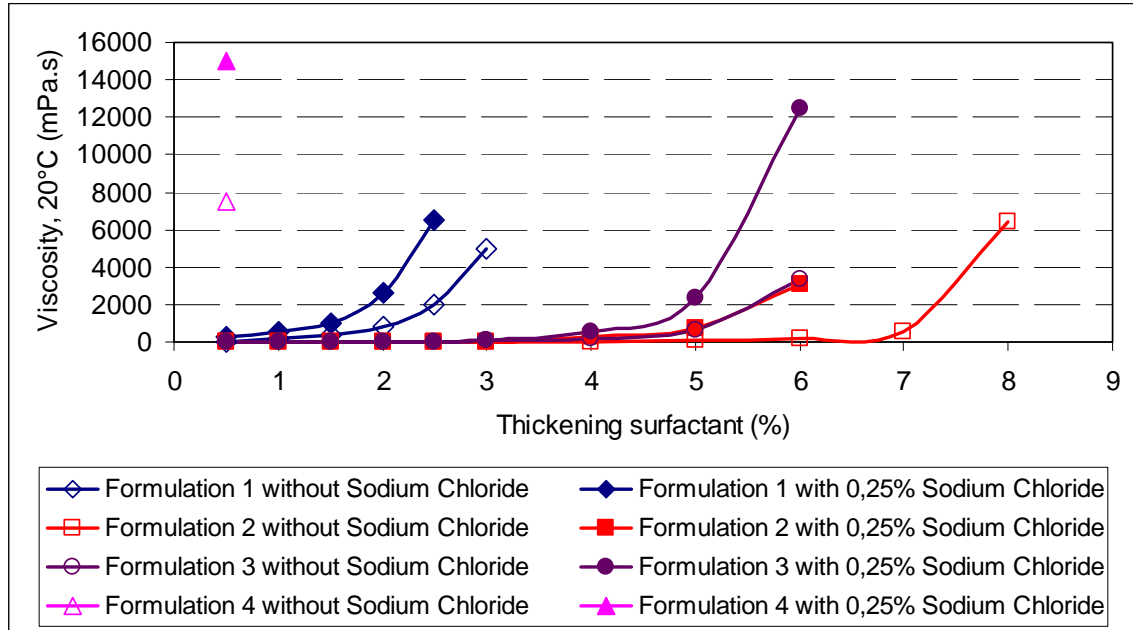
Graph 4: Viscosity variation in function of amount of Sodium Chloride

In above described more realistic conditions, the blend of Cocamide MIPA and low ethoxylated fatty alcohol shows a thickening profile similar to Cocamide DEA. PEG-4 Rapeseedamide shows a more important thickening response upon addition of electrolyte. A one for one replacement of Cocamide DEA in a basic formulation, from viscosifying point of view, may most probably be achieved by a well optimized product based on Cocamide MIPA and Laureth-4.

In a last series of tests, the selected alternative for Cocamide DEA (Cocamide MIPA (and) Laureth-4) is being evaluated in different common surfactant solutions (with and without electrolyte).

Formulation details Ingredients	Formula 1 Amount (% active)	Formula 2 Amount (% active)	Formula 3 Amount (% active)	Formula 4 Amount (% active)
Water	to 100	to 100	to 100	to 100
Sodium Laureth Sulfate	7.5	11	-	11
Sodium C14-16 Olefin Sulfonate	-	-	11	-
Cocamidopropyl Betaine	-	-	4	4
Lauryl Glucoside	-	4	-	-
Sodium Cocoamphoacetate	4	-	-	-
Disodium Laureth Sulfosuccinate	4	-	-	-
Citric Acid or Sodium Hydroxide	to pH 6.0	to pH 6.0	to pH 6.0	to pH 6.0
Cocamide MIPA (and) Laureth-4	see graph	see graph	see graph	see graph
Sodium Chloride	0 or 0.25	0 or 0.25	0 or 0.25	0 or 0.25

Table 7: Formulation details



Graph 5: Performance of best alternative in common surfactant systems

Selected thickening surfactant viscosifies easily common surfactant systems as shown in graph 5 including formulations containing sulfosuccinates or alkyl glucosides.

Conclusion

Numerous thickeners are available to cosmetic formulators in order to enhance the viscosity of foaming cosmetic products going from classical hydrocolloids to polymeric high MW surfactants and low MW nonionics or diethanolamine free alkanolamides. Although there are so many raw materials to choose from, the direct replacement of Cocamide DEA remains a difficult task.

The comparative study illustrates the superiority of one of the selected alternatives from point of view of workability and viscosity build-up performance in a formulation: it is an easy to handle liquid product based on Cocamide MIPA and Laureth-4 that gives a similar viscosity profile as Cocamide DEA at all tested conditions.

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