

# Amphoteric Anionic Interactions

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**KEY WORDS:** *surfactant interactions, anionic surfactants, amphoteric surfactants, foam, viscosity, salt curve, betaine*

**ABSTRACT:** *A study of interactions between anionic surfactants and amphoteric surfactants in solution demonstrates that betaines and anionic surfactants interact to have positive effects on viscosity, foam and the salt curve.*

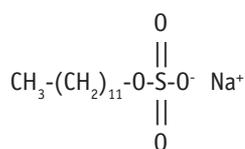
The interaction that occurs when combining the raw materials used in the formulation of personal care products is more than the sum of the properties of each of the raw materials. There are a number of interactions that include formation of self-assembling complexes. These complexes can either strengthen or weaken the functional attributes of the formulation. Because most of today's high performance formulations are very complex and contain a plethora of ingredients, it is difficult to predict the effect of changes in those formulations. In an attempt to understand these interactions, a simple system is used. The results of these interactions then can be used to help formulate more effective products.

## Surfactants

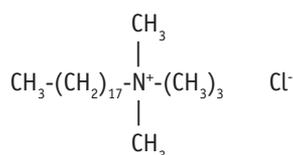
Surface active agents, commonly called surfactants, can be divided into groups depending upon the charge on the organic portion of the molecule.<sup>1</sup> According to such a scheme, surfactants are classified as anionic, cationic, non-ionic or amphoteric, with the charges as shown in Figure 1.

These materials are used in a variety of formulations and rarely are used alone. A look at a typical shampoo bottle will show numerous materials that all interact, in many instances producing viscosity-altering nanostructures. It is the nature of these interactions that make formulations work or fail. Consequently, it is helpful to understand the interactions between the groups. More than two decades ago, Ken Klein suggested the possibility of maximizing the effect of the interaction. The present article results from an attempt to understand these interactions.

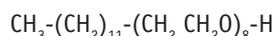
**Anionic ( - charge)** Sodium lauryl sulfate



**Cationic (+ charge)** Stearyl trimethyl ammonium chloride



**Non-ionic (no charge)** Laureth-8



**Amphoteric (+/- charge)** Stearyl betaine

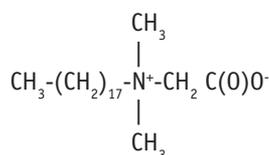


Figure 1. Surfactant classes, according to charge

**Materials with anionic-cationic interactions:** A common misunderstanding is the interaction between anionic and cationic materials. Formulators mixed stearylalkonium chloride and sodium lauryl sulfate and observed the white, pasty gunk that results. The nature of such interactions and maximizing the effect in formulation is an important aspect of formulation science.

The interaction of cationic and anionic surfactants were investigated in a previous study.<sup>2</sup> In that work, two types of quats, one hard and the other soft, were defined. Hard quats were those products that were incompatible with anionic surfactants. On the other hand, soft quats were defined as those quats that formed thick, clear, high-foaming complexes with anionic surfactants. There were differences in the hardness of the anionic surfactants, with sodium laureth-2-sulfate (SLES-2) being more compatible with quats than sodium lauryl sulfate (SLS).

The nature of water and the hydrogen bonding that occurs between molecules of water makes water a unique material that is essential to life as it is known. The interaction of ionic surfactants in dilute aqueous solution is important in formulation and utilization of personal care products.

## The interaction of ionic surfactants in dilute aqueous solution is important in formulation and utilization of personal care products.

Surfactants that possess charges can be selected and combined to form self-assembling units. These units are important to the functionality of these materials, forming useful nanostructures. The first step is to engineer the polymer using well-known techniques. The driving force for assembly is obtaining the lowest free energy in the system. Many times the lowest free energy state is not the least-ordered, but rather the most-ordered system. This particularly

**Table 1. Surfactants used in this study of interactions**

Charge	Description	Abbreviation	CAS #
Anionic	Sodium lauryl sulfate	SLS	151-21-3
Anionic	Sodium laureth-2 sulfate	SLES-2	3088-31-1
Amphoteric	Cocamidopropyl betaine	CAB	61789-40-4
Amphoteric	Dimer amido propyl betaine	DAB	(pending)
Amphoteric	Cetyl betaine	PB	693-33-4
Amphoteric	Lauric myristic amido betaine	LMAB	4292-10-8
Amphoteric	Lauramphopropionate	LP	14960-06-6
Amphoteric	Coco betaine	CB	68424-94-2

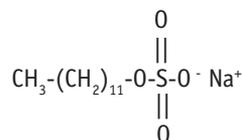
is true in aqueous systems where oil floats on water.

Because anionic and cationic materials have an opposite charge, they will attract each other and form a salt complex. It is the nature of this complex, rather than the properties of the surfactants themselves, that determines how the formulations function. As ionic materials are added to water, opposite charges attract and the same charges repel. As the concentration of point charges increases, the solution becomes so ordered that: (a) the solubility product of the salt is exceeded and a precipitate occurs, or (b) the viscosity of the solution increases, or (c) the complex becomes insoluble. The nature of this interaction is the focus of the present study.

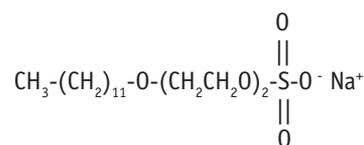
The current authors distinguish between two types of complexes that are made of anionic and cationic surfactants in aqueous solution. Those that thicken and remain clear are identified by the term *soft complexes*, while insoluble complexes are referred to as *hard complexes*. The chemical structure of each determines the hardness or softness of the complex. As a 10% active cationic surfactant is titrated into a 10% active solution of an anionic, such as SLS, more and more of the cationic surfactant complexes with the anionic. As the number of anionic and cationic species becomes equal, the number of interaction complexes will be greatest and at the same point, the concentration of uncomplexed surfactant becomes lowest. For this reason, the highest viscosity of the blends of anionic and cationic surfactant occurs at roughly equal amounts.

**Materials with anionic-amphoteric interactions:** The objective of this ar-

### Sodium Lauryl Sulfate (SLS)



### Sodium Laureth-2-Sulfate (SLES-2)



**Figure 2. Structures of tested anionic surfactants**

ticle is to expand the study of interactions to include several amphoteric surfactants, including betaines, amido betaines, and aminopropionate surfactants. Because amphoteric surfactants have both a positive and negative charge on the structure, the interactions were thought to be somewhat different than the interactions between quats, which have only a positive charge on the structure.

## The Surfactants

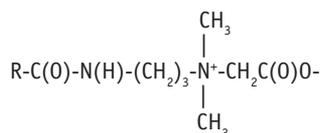
To study the interactions between anionic and amphoteric interactions, the surfactants chosen were the most traditional surfactants in the cosmetic industry. They are listed with their abbreviations and CAS numbers in Table 1. All surfactants were obtained from a commercial supplier<sup>a</sup>.

The anionic surfactants chosen were SLS and SLES-2 (Figure 2 on page 68).

<sup>a</sup> Colonial Chemical, South Pittsburg, Tenn.

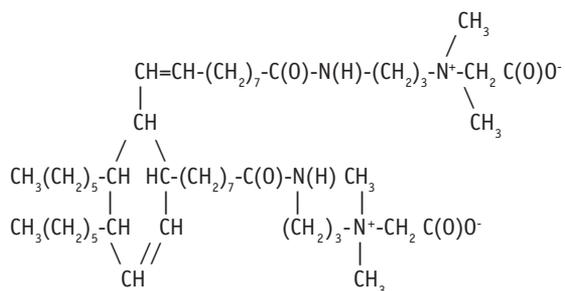


### Cocamidopropyl betaine (CAB)

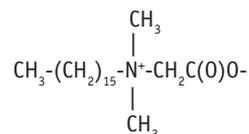


R is derived from coco.

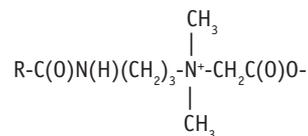
### Dimer amido propyl betaine (DAB)



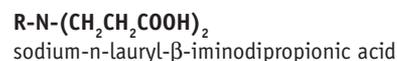
### Cetyl Betaine (PB)



### Lauric Myristic Amido Betaine (LMAB)



### Lauramphopropionate (LP)



### Coco Betaine (CB)

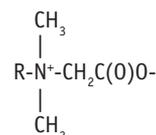


Figure 3. Structures of tested amphoteric surfactants



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Many amphoteric surface active agents could be evaluated in the study. For simplicity, the ones chosen were betaines and propionates (Figure 3), two classes of compounds that are important to the personal care market. Candidates were chosen in each class.

The protocol used was one in which surfactants were diluted to 10% actives in order to evaluate the interactions.

## A Viscosity Study

**Methodology:** In the protocol used, the surfactants first were diluted to 10% before evaluating the interactions. The protocol calls for these steps:

1. Prepare a 10% solution of anionic.
2. Prepare a 10% solution of amphoteric.
3. Prepare blends at 25:75, 50:50 and 75:25 by weight.
4. Run viscosity at 60 rpm, 30 rpm and 6 rpm using a Brookfield viscometer LV Spindle 4.

**Results:** The results are shown in Tables 2 and 3. No viscosity build was noted at any ratio using LP and either SLS or SLES-2.

**Table 2. Viscosity of SLS blends at selected blend ratios and RPM**

Blend	RPM	Viscosity at selected blend ratios		
		25:75	50:50	75:25
CAB:SLS	60	5	5,850	3,950
	30	4	12,000	7,900
	6	4	31,500	39,500
DAB:SLS	60	5	4,800	2,000
	30	4	8,100	2,800
	6	4	14,000	6,000
PB:SLS	60	7		9,650
	30	7	SPLIT	11,400
	6	7		23,000
LP:SLS	60	4	4	4
	30	4	4	4
	6	4	4	4
LMAB:SLS	60	6	4,100	57
	30	6	6,900	57
	6	6	14,500	55
CB:SLS	60	13	218	367
	30	13	361	365
	6	20	1,250	375

**Conclusions:** There are significant differences in the degree of interactions occurring between anionic surfactants

and amphoteric surfactants depending upon the nature of the amphoteric surfactant studied. Amino propionates



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exhibit no interaction. Alkyl betaines exhibit some interaction, but can become insoluble as the concentration approaches stoichiometric. Amido-betaines have strong interactions and better solubility, enabling production of gels.

Likewise, there are differences in the degree and direction of the interactions that occur between amphoteric surfactants and SLS or SLES-2. The effect of going from SLS to SLES-2 is variable and determined by the exact solubility of the amphoteric evaluated.

The nature of the interaction causes the observed differences in clarity and viscosity. The interactions can be classified as shown in Table 4.

## A Foam Study

Because in all instances the 50:50 blends had the highest viscosity, a 1% active solution of the 50:50 blends was subjected to the Ross-Miles Foam Height test<sup>b</sup>. For example, the 50:50 blend of CB:SLS produced a foam height of 250 mm, 225 mm and 185 mm at the immediate, 1 min and 5 min times, respectively, and a Draves wetting score of 8.8 sec. Results for the other nine blends tested and for SLS and SLES-2 alone are available at [www.CosmeticsandToiletries.com](http://www.CosmeticsandToiletries.com). Table 5 summarizes the results on the initial foam heights.

It was a surprise that SLS and SLES-2 appear near the bottom of the list, meaning that including betaine had a synergistic effect upon the foam. Even the combination with lowest foam was comparable to SLS. This result means there is a wide possibility to formulate products that have outstanding foam using blends of anionic and amphoteric surfactants. It also implies that the complex so formed has different foam properties than the SLS or SLES-2 alone. This explains why betaines are so commonly used in personal care formulation. They improve foam, an attribute that is very important to the consumer.

The Draves wetting test measures the amount of time it takes for a 1% solution

<sup>b</sup> The Ross-Miles Test is a standardized method (ASTM 1173) issued by an international testing company, ASTM International, West Conshohocken, Penn. USA.

**Table 3. Viscosity of SLES-2 blends at selected blend ratios and RPM**

Blend	RPM	Viscosity at selected blend ratios		
		25:75	50:50	75:25
CAB:SLES-2	60	11	2,550	10
	30	10	3,200	9
	6	10	3,500	9
DAB:SLES-2	60	6	1,700	3,000
	30	4	3,800	5,100
	6	4	14,500	18,500
PB:SLES-2	60	6.5	1,200	5,430
	30	5	1,620	7,160
	6	5	3,400	12,000
LP:SLES-2	60	10	10	10
	30	10	10	10
	6	10	10	10
LMAB:SLES-2	60	9	4,100	120
	30	7	6,700	120
	6	5	13,500	100
CB:SLES-2	60	367	3,700	7
	30	7,200	7,200	7
	6	28,800	28,800	2

**Table 4. Complex interactions**

Property	Insoluble complex	Marginally soluble	Soft complex	Soluble complex
Viscosity	Low	Some viscosity	High	Low
Appearance	Solid chunks	Milky	Clear	Clear
Example	PB:SLS (50:50)	PB:SLS (25:75)	DAB:SLES-2 (50:50)	LP:SLS-2 (50:50)

**Table 5. Initial foam (from highest to lowest)**

Material	Foam (mm)
CB:SLS	250
CB:SLES-2	200
CAB:SLS	200
CAB:SLES-2	200
LMAB:SLS	195
PB:SLES-2	190
LMAB:SLES-2	180
SLS	180
SLES-2	175
DAB:SLS	175
DAB:SLES-2	160

**Table 6. Wetting (from fastest to slowest)**

Material	Wetting (sec)
LMAB:SLS	2.9
CAB:SLS	3.0
PB:SLES-2	3.1
CAB:SLES-2	3.3
CB:SLS	4.0
SLS	4.8
CB:SLES-2	8.8
LMAB:SLES-2	12.4
SLES-2	12.4
DAB:SLS	39.5
DAB:SLES-2	42.1

of surfactant to cause a cotton skein to sink. Consequently, the lower the time required to sink, the better the wetting.

The wetting times of the blends (Table 6) vary quite a bit depending

upon the betaine used. The addition of all but the DAB material improved the wetting time of both SLS and SLES-2. The DAB products are much slower in terms of wetting time. This is not

**Table 7. Control salt curve data for SLS (100%)**

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	4
0.5	LV 1	60	4
1.0	LV 1	60	4
1.5	LV 1	60	5
2.0	LV 1	60	12
2.4	LV 1	60	50
3.0	LV 2	60	362
3.5	LV 3	30	2,120
4.0	LV 4	12	17,000
4.5	LV 4	12	19,500
5.0	LV 4	12	7,000
5.5	LV 3	30	2,060

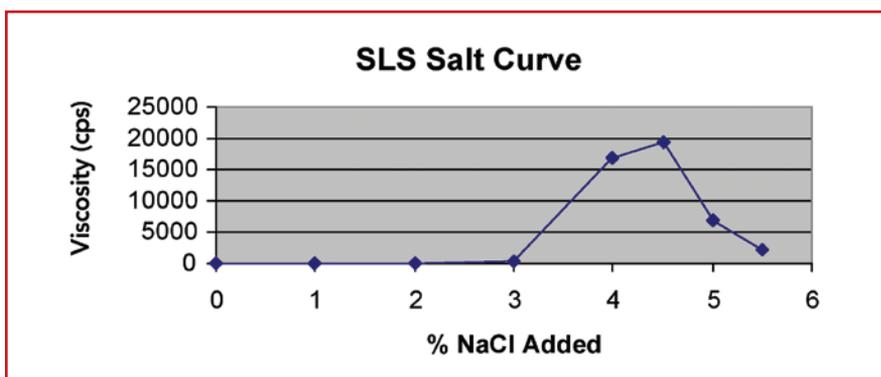


Figure 4. SLS salt curve

**Table 8. Peak viscosity from salt curve data for blends of SLS at 75% and selected amphoteric surfactants at 25%**

Blend	Peak Viscosity (cps)	% NaCl Added
DAB:SLS	37,500	3.0
CAB:SLS	37,000	3.5
LMAB:SLS	23,000	3.5
PB:SLS	22,500	2.5
SLS	19,500	4.5
CB:SLS	18,600	2.0

unexpected, because they are the most substantive products evaluated and provide outstanding conditioning not seen in combinations of anionic and other betaines.

### A Salt Addition Study

A standard method employed in formulation of cosmetic products is a so-called salt curve. Salt is added in increments and the viscosity is tracked with each add. There will be an increase,

but at a certain point the maximum viscosity will be reached, then the viscosity will drop. This is why the addition of water to a shampoo formulation might actually increase viscosity. Two salient attributes of the salt curve are important: the maximum viscosity and the amount of salt needed to reach it.

**Procedure:** Salt additions were made to the 10% solid blends consisting of 75% anionic and 25% betaine to determine peak viscosity. This ratio was

chosen for two reasons: a) the viscosity of the 50:50 blend already was high in most instances, and b) the 25% amphoteric : 75% anionic blend was more interesting commercially in terms of formulation cost.

Increments of 0.5% salt were added at a time to a 10% active solution of the specified blend. The viscosity was measured with a viscometer<sup>c</sup> after every addition at 22.0±0.3°C.

**Results:** Table 7 and Figure 4 give an example of the type of data obtained for SLS and used as a control. Similar data for SLES-2 and the ten blends tested are available at [www.CosmeticsandToiletries.com](http://www.CosmeticsandToiletries.com).

The amount of salt needed to reach peak viscosity dropped when betaine is present. In many instances the curve also was broadened.

**Conclusion:** As Table 8 indicates in summarizing the peak viscosity data for SLS, the addition of betaine and salt to the SLS resulted in improved peak viscosity in all cases except the CB betaine. In all instances, addition of betaine shifted the salt curve to the left. In other words, the amount of salt needed to reach peak viscosity dropped when betaine is present. In many instances the curve also was broadened. The presence of the conditioning betaine DAB actually increased peak viscosity and lowered the amount of salt needed to reach it in SLS systems and did so without adverse effect upon foam.

Table 9 (on page 74) indicates that the addition of betaine and salt to the SLES-2 resulted in lowering of the peak viscosity in all cases. LMAB decreased peak viscosity least. In all instances the addition of betaine shifted the salt curve to the left, demonstrating again that the amount of salt needed to reach peak viscosity dropped when betaine is present. The inclusion of the conditioning

<sup>c</sup> Synchro-lectric, Brookfield

betaine DAB provided good viscosity and conditioning.

## Conclusion

The combination of betaines and anionic surfactants is a powerful tool to the formulator to provide value-added formulations. This study looked at only a few of those value-added attributes. Others include conditioning, foam thickness and bubble structure, and feel on the skin. All these properties will benefit by proper selection of a betaine.

The formulator should investigate such interactions and maximize them for the specific formulation goals desired.

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Send e-mail to Tolenick@mindspring.com.

1. AJ O'Lenick, Surfactants Strategic Raw Materials, Carol Stream, Illinois: Allured Publishing (2004) p 1
2. Ibid, p 112

C&T

**Table 9. Peak viscosity from salt curve data for blends of SLES-2 at 75% and selected amphoteric surfactants at 25%**

Blend	Peak Viscosity (cps)	% NaCl Added
SLES-2	25,000	5.5
LMAB:SLES-2	24,000	3.0
DAB:SLES-2	19,250	2.5
CB:SLES-2	18,500	2.5
CAB:SLES-2	15,750	2.0
PB:SLES-2	15,200	2.5

## RHEOLOGY OF COMPLEX

While the peak viscosity is a measure of the interaction of the anionic and amphoteric surfactants, the resistance to shear is a measure of the stability of the complex.

The term Newtonian describes a material in which a linear relationship exists between shear stress and shear rate. In Newtonian fluids (typically water and solutions containing only low-molecular-weight material) the viscosity is independent of shear strain rate.

The term pseudoplastic is used to describe a material that experiences a decrease in viscosity with increasing shear rate (a process called shear-thinning). Pseudoplastic materials instantaneously decrease in viscosity with increase in shear strain rate (also called flow) and are therefore easier to pump and mix. They are shear-thinning. This often is a consequence of high-molecular-weight molecules being untangled and oriented by the flow. Generally this behavior increases with concentration.

A specific type of pseudoplastic material is a thixotropic liquid. It exhibits a time-dependent response to shear strain rate over a longer period than that associated with changes in the shear strain rate. These materials may liquefy on being shaken and may or may not solidify when the shaking has stopped.

The term dilatant is used in common practice to refer to a material that increases in viscosity as shear rate increases (a process called shear-thickening).

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