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Surfactant Interactions

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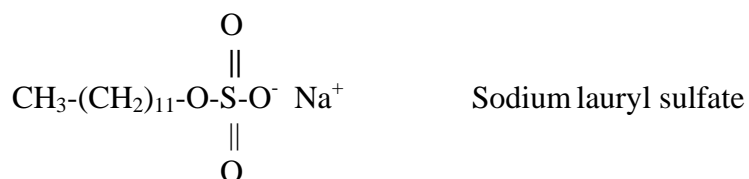
Abstract

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 which include formation of self assembling complexes. These complexes can either enhance or detract from the functional attributes of the formulation. Since most of today's high performance formulations are very complex containing a plethora of ingredients, it is difficult to predict the effect of changes in those formulations. In an attempt to understand these interactions we have gone back to simple systems. The results of these interactions can then be used to help formulate more effective products.

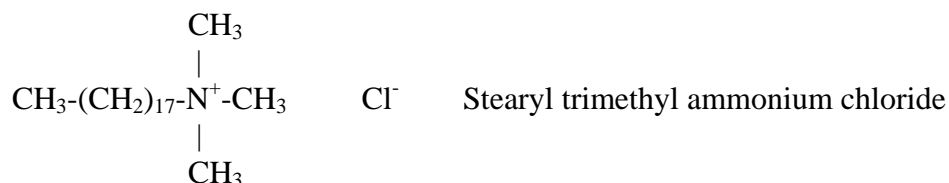
Surfactants

Surface active agents, commonly called surfactants, can be divided into groups depending upon the charge on the organic portion of the molecule¹. According to such a scheme surfactants are classified as:

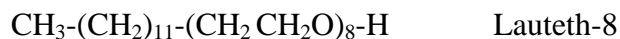
Anionic (- charge)



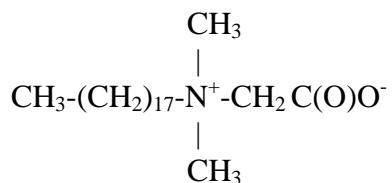
Cationic (+ charge)



Non-ionic (no charge)



Amphoteric (+/- charge)



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 together which all interact, in many instances producing viscosity altering nanostructures. It is the nature of these interactions that make our formulations work or fail. Consequently, it is helpful to understand the interactions between the groups. Ken Klein has suggested the possibility of maximizing the effect of the interaction as far back as the late 1970s. This paper is a result of our attempt to understand these interactions.

Most commonly understood is the interaction between anionic and cationic materials. Most formulators put stearylalkonium chloride and sodium lauryl sulfate together 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. In a previous study² we investigated the interaction of cationic and anionic surfactants. In that work we defined two types of quats, one hard and the other soft. Hard quats were those products which were incompatible with anionic surfactants. Soft quats on the other hand, 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 SLES-2 (Sodium lauryl sulfate) being more compatible with quats than SLS (sodium lauryl sulfate).

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 we know it. 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 is particularly true in aqueous systems, where oil floats on water.

Since 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 are increased, the solution becomes so ordered that either (a) the solubility product of the salt is exceeded and a precipitate occurs, (b) The viscosity of the solution increases or (c) the complex becomes insoluble. It is the nature of this interaction that is of interest to the present study. We have dubbed complexes that are made of anionic and cationic surfactants in aqueous solution that thicken and remain clear 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, like sodium lauryl sulfate, 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. It is for this reason that the highest viscosity of the blends of anionic and cationic surfactant occurs at roughly equal amounts.

Rehology 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 (shear-thinning). Pseudoplastic materials instantaneously decrease in viscosity with increase in shear strain rate (*e.g.* flow) and are therefore easier to pump and mix. They are shear-thinning. This is often 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 exhibit a time-dependent response to shear strain rate over a longer period than that associated with changes in the shear strain rate. They 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 material that increases in viscosity as shear rate increases, that is they are shear-thickening.

The objective of this paper is to expand the study of interactions to include several amphoteric surfactants including, betaines, amido betaines and aminopropionate surfactants. Since 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 them.

Surfactants Chosen

The surfactants chosen were the most traditional surfactants in the cosmetic industry.

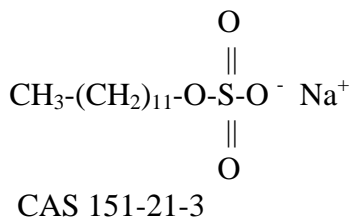
Anionic Surfactants

The anionic surfactants chosen for study in this paper were:

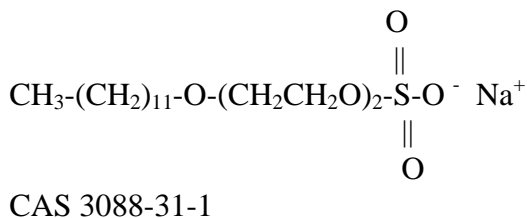
Designation	Description
S-1	SLS
S-2	SLES-2

Structures:

S-1 Sodium Lauryl Sulfate (SLS)



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



These products were obtained commercially from Colonial Chemical So. Pittsburg, Tn.

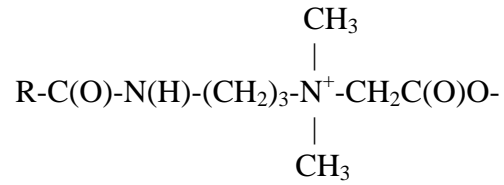
Amphoteric Surfactants

There are a large number of amphoteric surface active agents that could be evaluated in the study. For simplicity we chose to look at betaines and propionates, two important classes of compounds to the personal care market. Candidates were chosen in each class. The amphoteric surfactants used in this study were:

Designation	Description	Abbreviation
A-1	Cocamidopropyl betaine	(CAB)
A-2	Dimer amido propyl betaine	(DAB)
A-3	Cetyl Betaine	(PB)
A-4	Lauric Myristic Amido Betaine	(LMAB)
A-5	Lauramphopropionate	(LP)
A-6	Coco Betaine	(CB)

Amphoteric Structures:

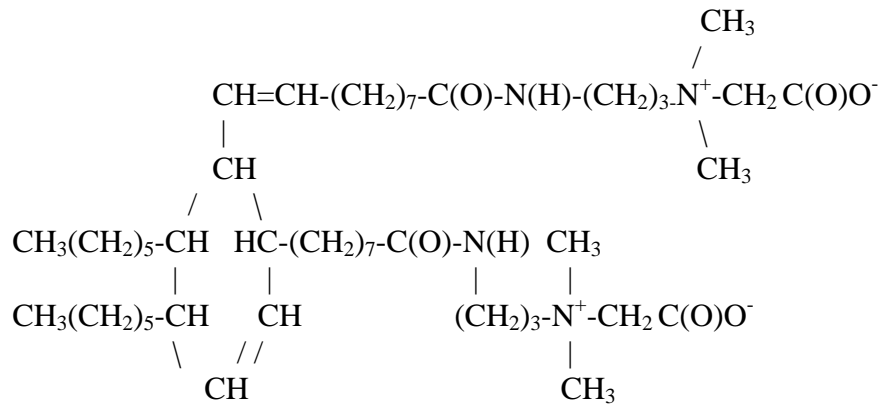
A-1 Cocamidopropyl betaine (CAB)



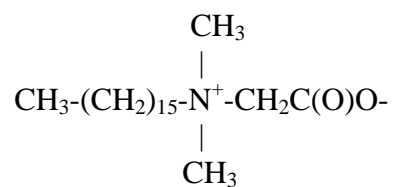
R is derived from coco.

CAS No. 61789-40-4

A-2 Dimer amido propyl betaine (DAB)

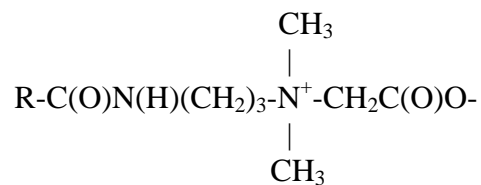


A-3 Cetyl Betaine (PB)



CAS 693-33-4

A-4 Lauric Myristic Amido Betaine (LMAB)



CAS 4292-10-8

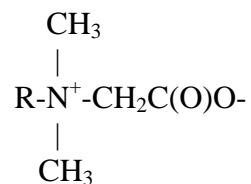
A-5 Lauramphopropionate (LP)



sodium-n-lauryl-β-iminodipropionic acid

CAS No. 14960-06-6

A-6 Coco Betaine (CB)



CAS 68424-94-2

These products were commercially obtained from Colonial Chemical So. Pittsburg, Tn.

I Anionic Interaction Study

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

Test Methodology:

1. A 10% solution of anionic was prepared.
2. A 10% solution of amphoteric was prepared
3. Blends at 25/75, 50/50 and 75/25 by weight were prepared.
4. Viscosity was run at 60 rpm, 30 rpm and 6 rpm using a Brookfield viscometer LV Spindle 4.

Results

A-1 CAB

CAB : SLS

Ratio	25/75	50/50	75/25
60 Rpm	5	5,850	3,950
30 RPM	4	12,000	7,900
6 RPM	4	31,500	39,500

COAB SLES

Ratio	25/75	50/50	75/25
60 Rpm	11	2,550	10
30 RPM	10	3,200	9
6 RPM	10	3,500	9

A-2 DAB

DAB:SLS

Ratio	25/75	50/50	75/25
60 Rpm	5	4,800	2,000
30 RPM	4	8,100	2,800
6 RPM	4	14,000	6,000

DAB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	6	1,700	3,000
30 RPM	4	3,800	5,100
6 RPM	4	14,500	18,500

A-3 Palmitic Betaine (PB)

PB:SLS

Ratio	25/75	50/50	75/25
60 Rpm	7		9,650
30 RPM	7	SPLIT	11,400
6 RPM	7		23,000

PB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	6.5	1,200	5,430
30 RPM	5	1,620	7,160
6 RPM	5	3,400	12,000

A-4 Lauramphopropionate

LP SLS

Ratio	25/75	50/50	75/25
60 Rpm	4	4	4
30 RPM	4	4	4
6 RPM	4	4	4

LP SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	10	10	10
30 RPM	10	10	10
6 RPM	10	10	10

No viscosity build was noted at any ratio using this amphoteric and either sodium lauryl sulfate or sodium lauryl ether sulfate.

A-5 Lauric Myristic Amido betaine

LMAB
SLS

Ratio	25/75	50/50	75/25
60 Rpm	6	4,100	57
30 RPM	6	6,900	57
6 RPM	6	14,500	55

LMAB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	9	4,100	120
30 RPM	7	6,700	120
6 RPM	5	13,500	100

A-6 Coco betaine

CB SLS

Ratio	25/75	50/50	75/25
60 Rpm	13	218	367
30 RPM	13	361	365
6 RPM	20	1,250	375

CB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	367	3,700	7
30 RPM	7,200	7,200	7
6 RPM	28,800	28,800	2

Conclusions

There are significant differences in the degree of interactions which occur between anionic surfactants and amphoteric surfactants depending upon the nature of the amphoteric surfactant studied. Amino propionates exhibit no interaction. Alkyl betaines exhibit some interaction but can become insoluble as the concentration approaches stoichiometric, amidobetaines have strong interactions and better solubility producing gels.

There are likewise 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.

Complex Interaction

The nature of the interaction causes the observed differences in clarity, and viscosity. The interactions can be classified as follows:

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 (50/50)	LP SLS (50/50)

B. Foam Data

Since in all instances the 50/50 had the highest viscosity a 1% active solution of the 50/50 blend was subjected to the Ross Miles test

Product	50/50 COAB/SLS	50/50 COAB/SLES-2	50/50 DAB/SLS	50/50 DAB/SLES-2
Immed (mm)	200	200	175	160
1 min (mm)	170	170	155	145
5 min (mm)	160	160	150	135
Draves (sec.)	3.03	3.34	39.50	42.1

Product	50/50 SLES-2/LMAB	50/50 SLS/LMAB	50/50 SLES-2/PB	50/50 SLES/PB
Immed (mm)	180	195	190	Insoluble
1 min (mm)	155	170	165	Insoluble
5 min (mm)	150	160	155	Insoluble
Draves (sec.)	12.41	2.90	3.10	Insoluble

Product	50/50 SLES-2/CB	50/50 SLS/CB	100 SLES-2	100 SLS
Immed (mm)	200	250	175	180
1 min (mm)	175	225	160	165
5 min (mm)	165	185	155	155
Draves (sec.)	4.0	8.8	12.4	4.8

Initial Foam (From highest to lowest)

Material	Foam
CB-SLES-2	250
COAB-SLS	200
COAB-SLES	200
CB-SLS	200
LMAB-SLS	195
LMAB-SLES	180
PB-SLES-2	190
SLES-2	180
SLS	175
DAB-SLS	175
DAB-SLES-2	160

It was a surprise that SLS and SLES-2 appear near the bottom of the list, meaning there is a synergistic effect of including betaine 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. It also implies that the complex so formed has different foam properties than the SLSD or SLES 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.

Wetting (From fastest to slowest)

We evaluated Draves wetting. The test measures the amount of time it takes for a 1% solution of surfactant to cause a cotton skein to sink. Consequently, the lower the time required to sink, the better the wetting.

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

The wetting times of the blends 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 unexpected, since they are the most substantive products evaluated and provide outstanding conditioning not seen in combinations of anionic and other betaines.

Salt Addition

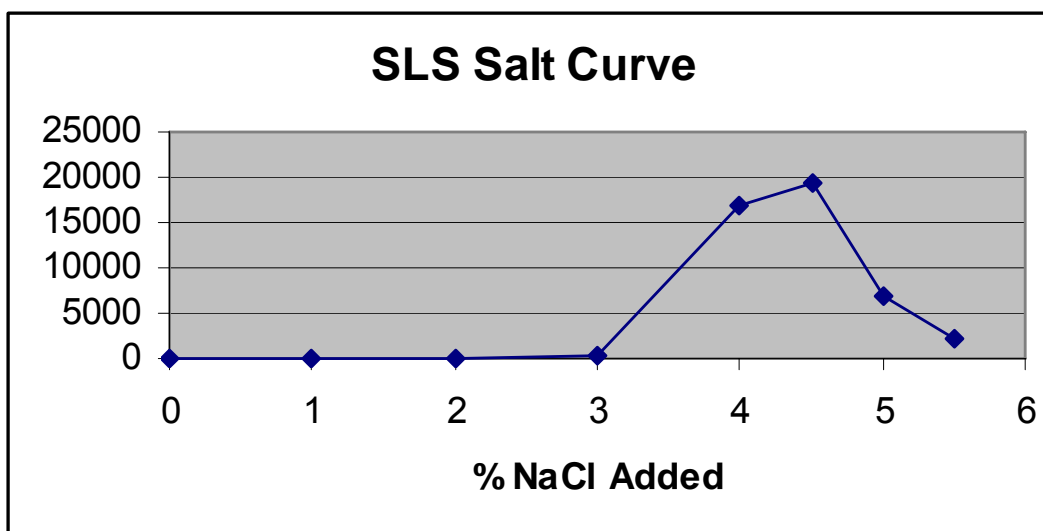
A standard method employed in formulation of cosmetic product is a so called salt curve. Salt is added in increments and the viscosity is tracked with each add. There will be an increase, but at a certain point the maximum viscosity will be reached, then the viscosity will drop. This is why the addition of water to a shampoo formulation might actually increase viscosity. Two salient attribute of the salt curve are important, the maximum viscosity and the amount of salt needed to reach it.

Salt additions were made to the 10% solids blends consisting of 75% anionic and 25% betaine to determine peak viscosity. This ratio was chosen for two reasons, first the viscosity of the 50 / 50 was already high in most instances, and second the 25% amphoteric 75% anionic was more commercially interesting 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 after every addition @ 22.0 ±0.3° C using a Brookfield Synchro-lectric^R Viscometer.

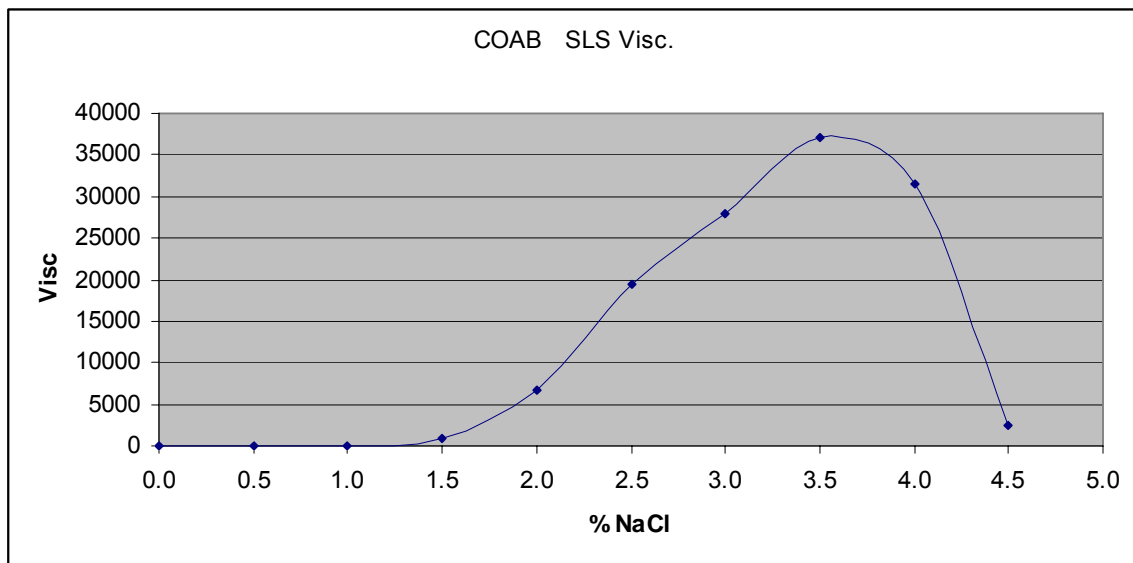
Control Salt Curve Data for SLS (100%)

% 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



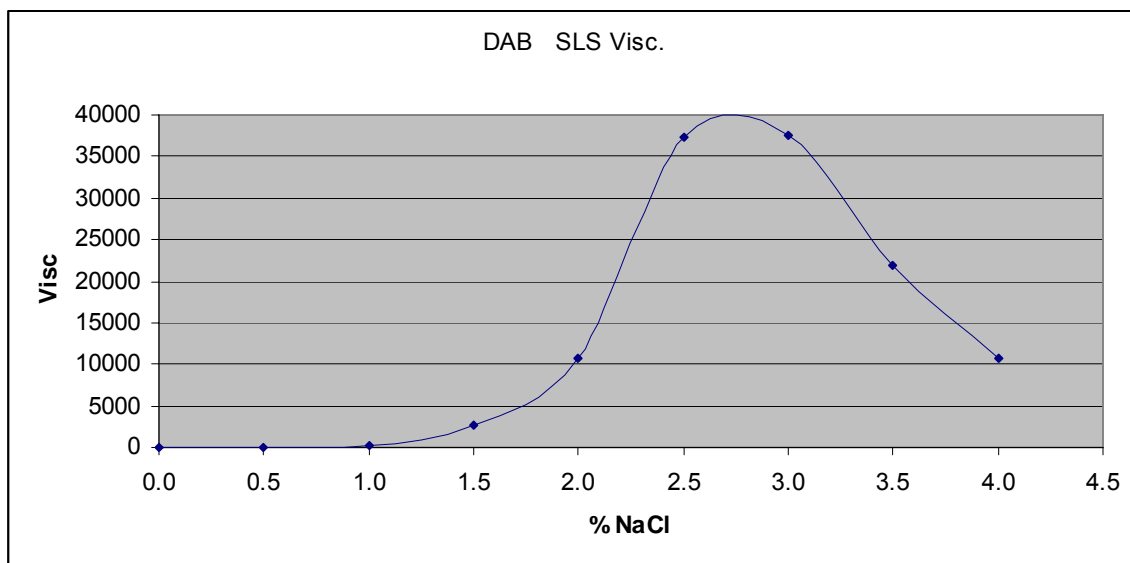
A-1 Salt Curve Data for SLS (75)/COAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	4
0.5	LV 1	60	8.5
1.0	LV 2	60	67.5
1.5	LV 3	30	880
2.0	LV 3	12	6,800
2.5	LV 4	12	19,500
3.0	LV 4	12	28,000
3.5	LV 4	12	37,000
4.0	LV 4	12	31,500
4.5	LV 4	12	23,250



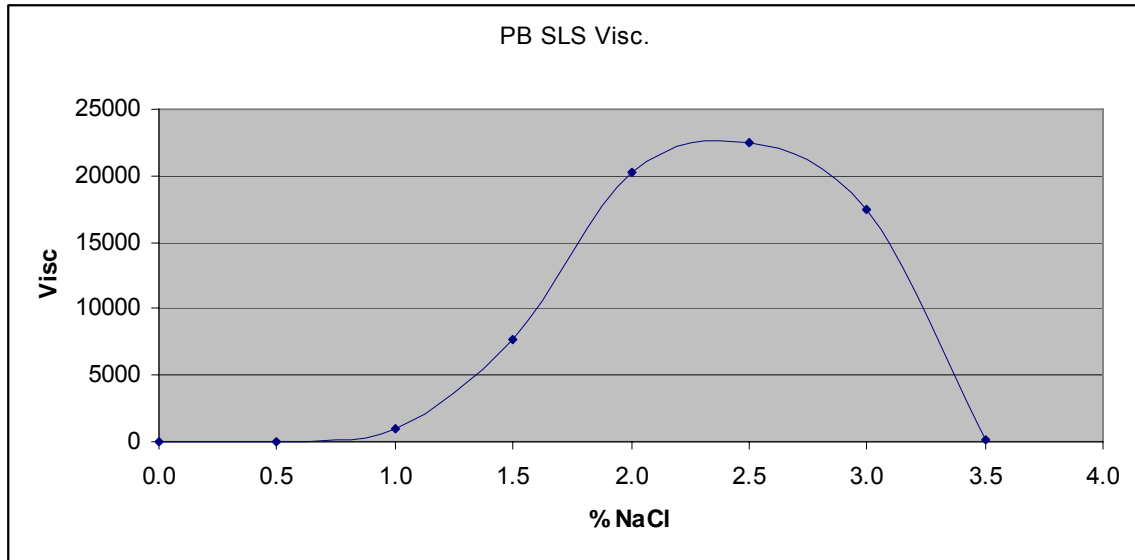
A-2 Salt Curve Data for SLS (75)/ DAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	5
0.5	LV 1	60	13
1.0	LV 2	30	165
1.5	LV 3	30	2,680
2.0	LV 4	12	10,800
2.5	LV 4	12	37,250
3.0	LV 4	12	37,500
3.5	LV 4	12	22,000
4.0	LV 4	12	10,750



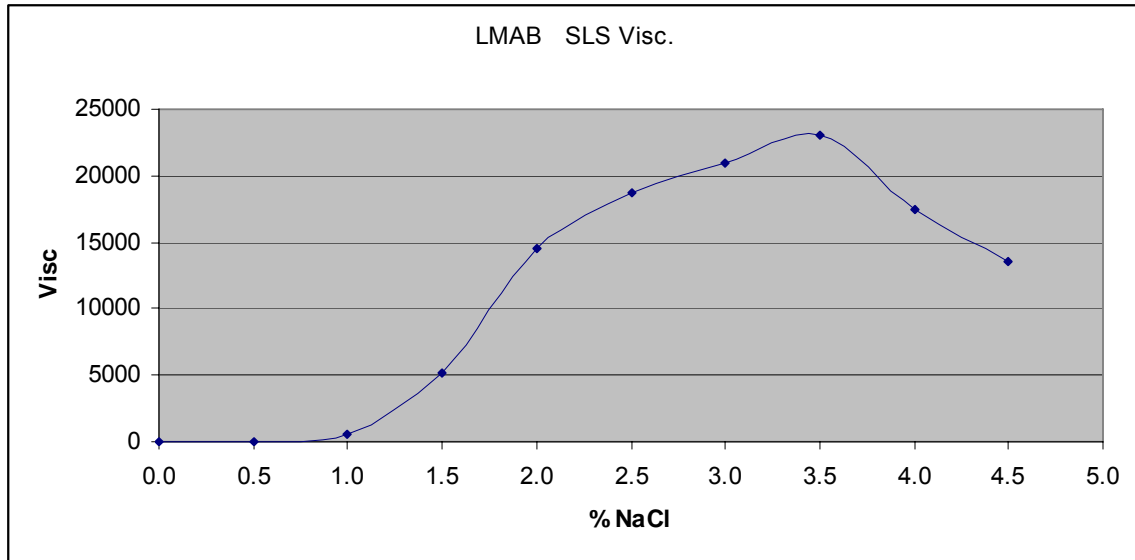
A-3 Salt Curve Data for SLS (75)/PB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 1	60	37
1.0	LV 2	12	1,012
1.5	LV 3	12	7,650
2.0	LV 3	12	20,250
2.5	LV 4	12	22,500
3.0	LV 4	12	17,500
3.5	LV 2	12	162



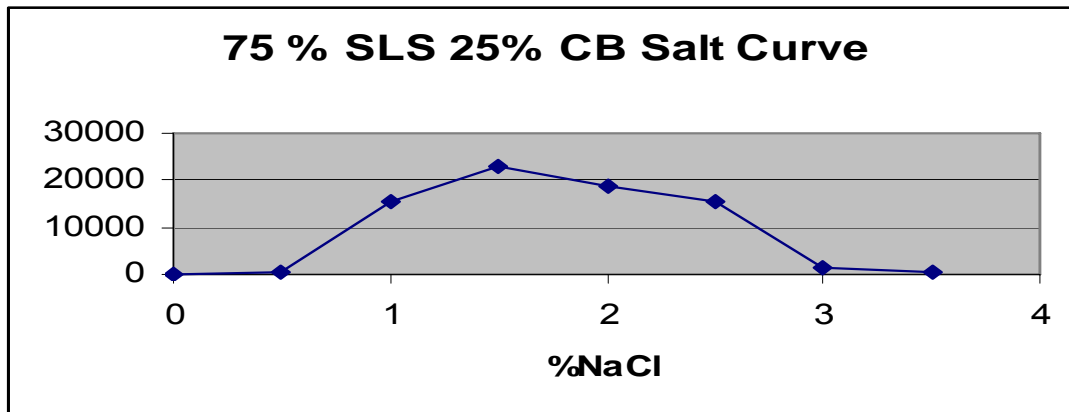
A-4 Salt Curve Data for SLS (75) / LMAB(25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	7
0.5	LV 1	60	34
1.0	LV 2	30	562
1.5	LV 3	30	5,150
2.0	LV 4	12	14,500
2.5	LV 4	12	18,750
3.0	LV 4	12	21,000
3.5	LV 4	12	23,000
4.0	LV 4	12	17,500
4.5	LV 4	12	13,500



A-5 Salt Curve Data for SLS (75) / CB(25)

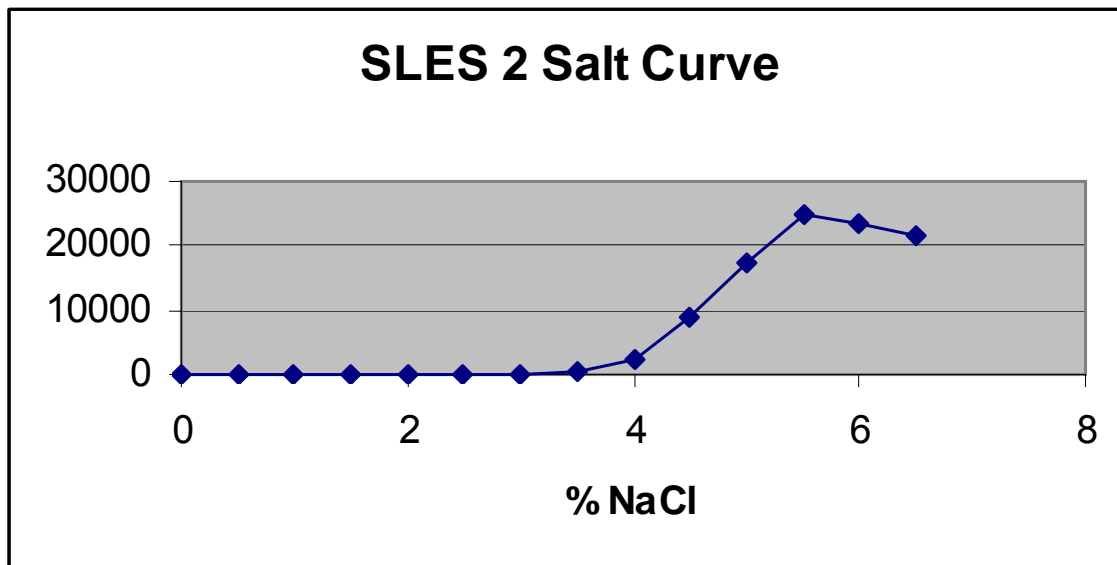
% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	20
0.5	LV 2	60	428
1.0	LV 4	12	15,500
1.5	LV 4	12	23,000
2.0	LV 4	12	18,600
2.5	LV 4	12	15,500
3.0	LV 3	30	1,620
3.5	LV 2	30	580



SLES-2 Salt Curves

Control Salt Curve Data for SLES-2 (100%)

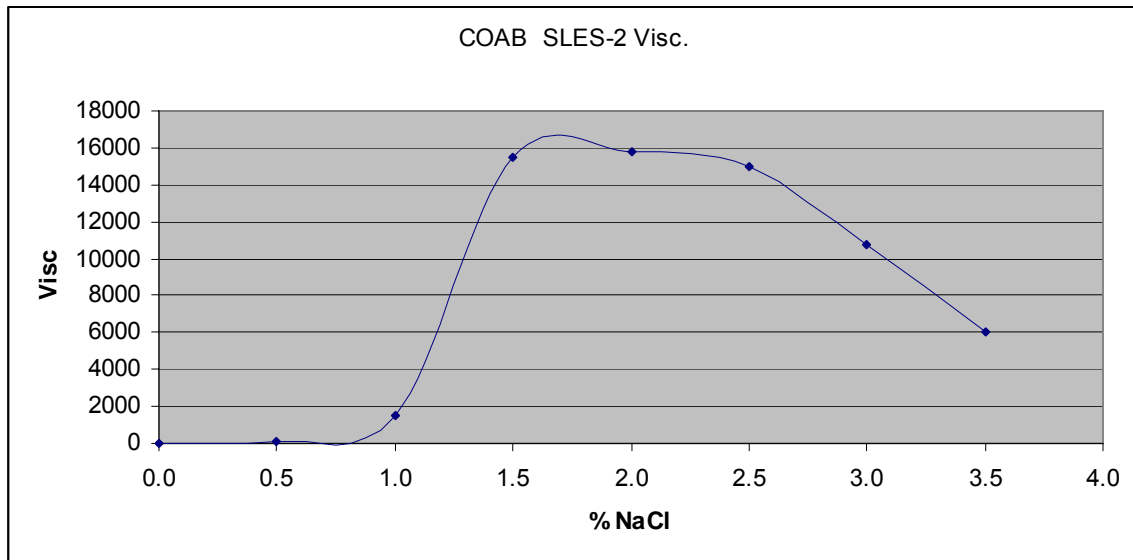
% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	4
0.5	LV 1	60	6
1.0	LV 1	60	6
1.5	LV 1	60	6
2.0	LV 1	60	7
2.5	LV 1	60	15
3.0	LV 1	60	67
3.5	LV 3	30	540
4.0	LV 3	12	2,204
4.5	LV 4	12	8,750
5.0	LV 4	12	17,250
5.5	LV 4	12	25,000
6.0	LV 4	12	23,250
6.5	LV 4	12	21,500



A large concentration of salt is needed to get to the peak viscosity.

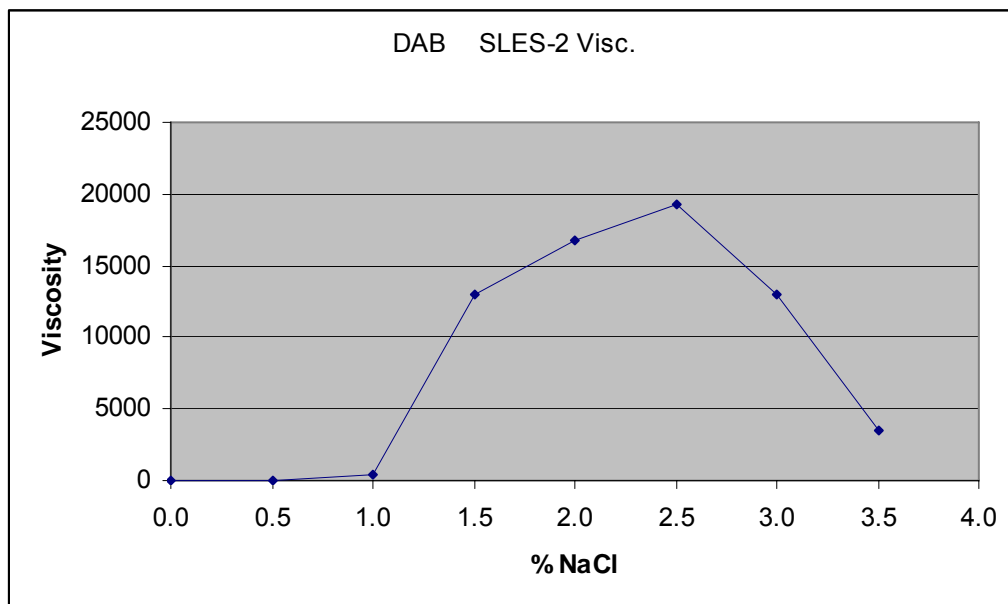
A-1 Salt Curve Data for SLES2 (75)/COAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	10
0.5	LV 2	60	95
1.0	LV 2	12	1,475
1.5	LV 4	12	15,500
2.0	LV 4	12	15,750
2.5	LV 4	12	15,000
3.0	LV 4	12	15,000
3.5	LV 4	12	10,750
4.0	LV 4	12	6,000



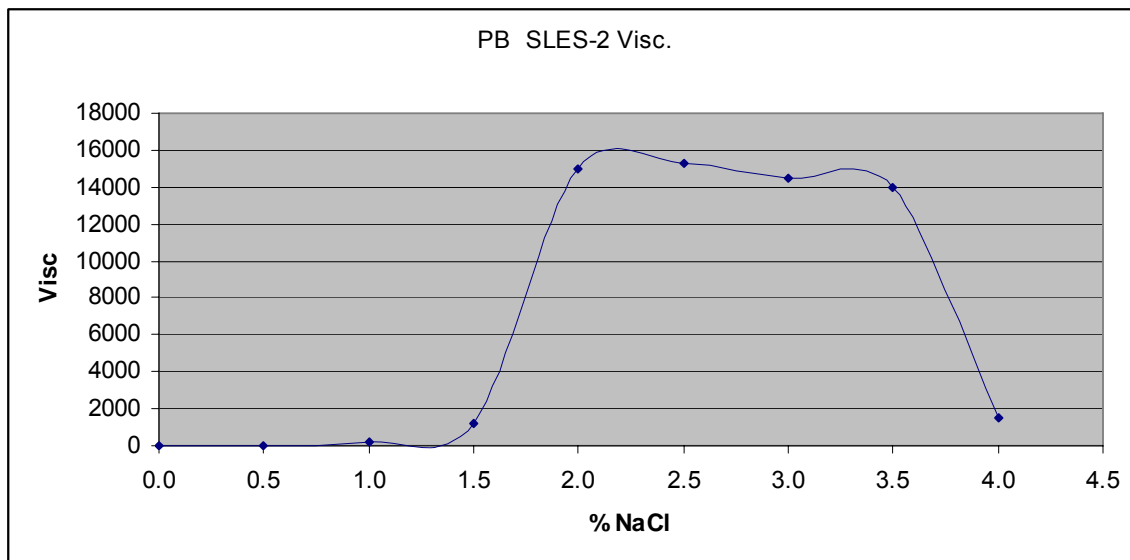
A-2 Salt Curve Data for SLES2 (75)/ DAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 2	60	30
1.0	LV 2	12	425
1.5	LV 4	12	13,000
2.0	LV 4	12	16,750
2.5	LV 4	12	19,250
3.0	LV 4	12	13,000
3.5	LV 4	12	3,500



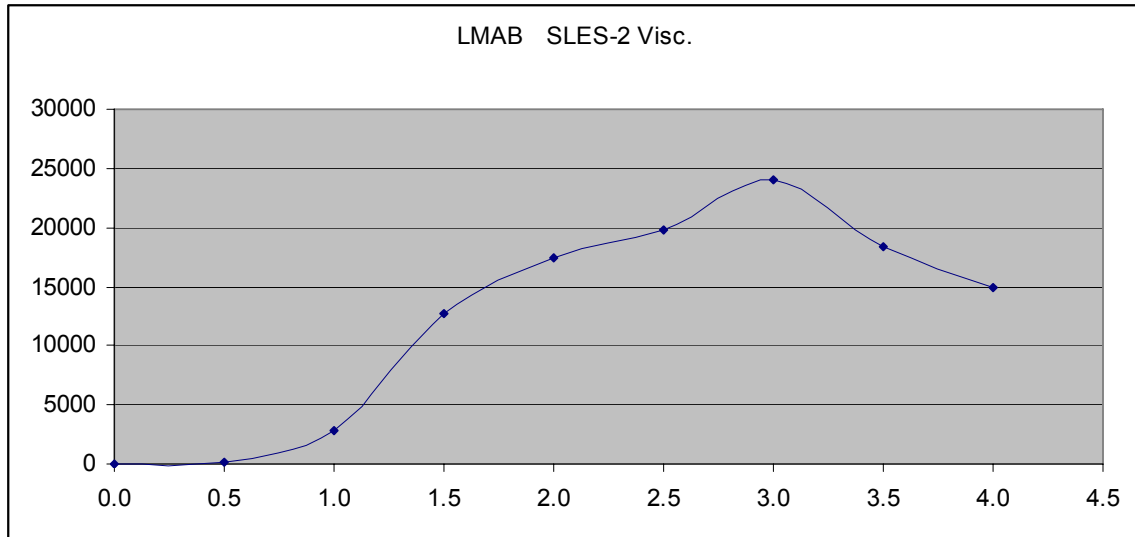
A-3 Salt Curve Data for SLES2 (75)/PB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 2	60	25
1.0	LV 2	30	175
1.5	LV 2	12	1,225
2.0	LV 4	12	15,000
2.5	LV 4	12	15,250
3.0	LV 4	12	14,500
3.5	LV 4	12	14,500
4.0	LV 4	12	1,500



A-4 Salt Curve Data for SLES2 (75) / LMAB(25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	9
0.5	LV 2	60	95
1.0	LV 4	12	2,750
1.5	LV 4	12	12,750
2.0	LV 4	12	17,500
2.5	LV 4	12	19,800
3.0	LV 4	12	24,000
3.5	LV 4	12	18,350
4.0	LV 4	12	15,000



A-5 Salt Curve Data for SLES2 (75) / CB(25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 1	60	24
1.0	LV 3	60	300
1.5	LV 4	12	4,500
2.0	LV 4	12	15,750
2.5	LV 4	12	18,500
3.0	LV 4	12	15,000
3.5	LV 4	12	6,000
4.0	LV 4	30	1,700

Conclusions

Peak Viscosity / Salt

SLS Materials

Material	Peak Viscosity	% NaCl Added
DAB-SLS	37,500	3.0
COAB-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

The addition of betaine and salt to the SLS resulted in improved peak viscosity in all cases but the CB betaine. Additionally, in all instances addition of betaine shifted the salt curve to the left. That is the amount of salt needed to reach peak viscosity dropped when betaine is present. In many instances the curve was also 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.

SLES-2

Material	Peak Viscosity	% 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
COAB-SLES-2	15,750	2.0
PB-SLES-2	15,200	2.5

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. That is the amount of salt needed to reach peak viscosity dropped when betaine is present. The inclusion of the conditioning betaine DAB provided good viscosity along with conditioning.

The combination of betaines and anionic surfactants provides a powerful tool to the formulator to provide value added formulations. We looked at only a few of such attributes. In addition to those we studied, foam thickness and bubble structure, feel on the skin and conditioning are all properties that will benefit by proper selection of a betaine. We encourage the formulator to investigate such interactions and maximize them for the specific formulation goals desired.

References

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