Enhancing the conditioning performance of cationic amino lipids by formulating for optimized lamellar gel networks

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Abstract (Maximum of 250 words (total max is 5000))

Background: Cationic amino lipids, such as Brassicyl Valinate Esylate (BVE), are a more sustainable alternative to traditional quaternary cationic surfactants such as Behentrimonium Chloride (BTAC). Cationic surfactants are typically formulated with long chain fatty alcohols (Falcs) to yield lamellar liquid crystalline (LC) systems suitable as effective hair conditioning products. The present study examined the effects of Falc on lamellar gel network (LGN) formation and properties when formulating with BVE in comparison to the industry benchmark, BTAC.

Methods: LC structure and morphology are characterized using polarized light microscopy, small- and wide-angle x-ray scattering, and rheology is used to quantify macroscopic fluid properties. Hair conditioning performance is assessed via instrumental testing on hair (wet/dry combing, static build up, contact angle) and consumer sensory perception.

Results: Previous studies examined combinations of BVE with Brassica Alcohol (BA: C18-C22 alkyl chain) showing lower levels of comb force reduction than BTAC with BA. In the present study, we demonstrate that the LGN formed by combining BVE with cetearyl alcohol (CSA: 50/50 mixture of C16/C18 alcohols) can provide equivalent conditioning performance to BTAC/CSA systems.

Conclusion: This study demonstrates that proper formulation of LGN systems enables cationic amino lipid conditioning agents, e.g. BVE, to deliver equivalent conditioning performance to traditional quats, e.g. BTAC. By varying the C-chain length and use level of the fatty alcohol, conditioning intensity can be modulated to deliver benefits that are desirable for specific hair types, e.g. lighter conditioning for fine hair vs. heavier conditioning for dry or damaged hair.

Keywords: Hair conditioning; cationic amino lipid surfactant; lamellar phase; sustainability

Introduction.

Cationic amino lipids have been established as a more sustainable alternative to traditional cationic surfactants due to their 100% renewable origin and superior human and environmental safety profiles. Unlike traditional quaternary ammonium cationic surfactants, i.e. "quats", used in hair care, amino lipids derive their cationic character from protonation of their primary amine moieties that are derived from natural amino acids. Like other long chain cationic surfactants, amino lipids such as Brassicyl Valinate Esylate (BVE) are typically formulated with long chain fatty alcohols to yield lamellar liquid crystalline (LC) systems that demonstrate significant viscosity and yield value. These LC systems can stabilize hydrophobic oil phases and exhibit strong substantivity to hair, making them highly effective as rinse-off and leave-on hair conditioning products.

Healthy hair is naturally lubricated due to the presence of an 18-methyleicosanoic acid (18-MEA) lipid layer on the surface of the intact cuticle [1] resulting in low frictional forces experienced during skin–hair interactions, hair–hair interactions, and interactions between the hair and grooming materials [3,4]. This provides a smooth feel in both wet and dry conditions as well as minimum hair breakage [2,3]. Frequent grooming, chemical/thermal treatments including e.g. washing and blow drying, and environmental exposure can lead over time to the stripping of the 18-MEA layer and damage to the cuticle cells [5] and subsequently, increased hair friction and breakage [4]. Hair conditioners are used to temporarily reduce friction forces by deposition of conditioning molecules. This deposition is facilitated by electrostatic interaction between hair's negative surface charge with the positively charged cationic surfactants present in hair conditioners [7]. Typical hair conditioners are formulated with cationic surfactants, fatty alcohols, water, and sometimes oils such as dimethicone or triglycerides [5]. Of these components, cationic surfactants and fatty alcohols serve as the formulation backbone, as they aid in the formation of the lamellar gel network (LGN) and provide the overall lubrication benefits of the conditioner [3].

The alkyl quaternary ammonium compounds (or alkyl quats) Behentrimonium Chloride (BTAC) and Cetrimonium Chloride (CTAC) are the most widely used alkyl quats in hair conditioner preparations [9]. However, such compounds are known to have poor biodegradability and have been reported present in wastewater and surface waters with the potential of impacting the environment negatively. Ingredients from renewable, plant-based sources with improved performance and decreased toxicity such as amino acid-based surfactants (AAS) are a promising class of ingredients due to their biocompatibility and biodegradability characteristics. Like alkyl quats, cationic AASs carry a positive charge on their hydrophobic head group making them substantive to hair [8]. The novel quat-free surfactant BVE is derived from 100% renewable raw materials, through a solvent-free process using no heavy metal catalysts. The cationic ammonium head group, derived from L-valine amino acid, is pre-neutralized with ethanesulfonic acid and linked, via a biodegradable ester linking group, to a lipophilic alkyl tail group, derived from natural Brassica Napus seed oil [10,11]. In general, amino lipids have superior safety and environmental profiles than conventional cationic surfactants [12]. Previous studies examined combinations of BVE with Brassica Alcohol (C18-C22 alkyl chain) showing somewhat lower levels of wet and dry comb force reduction as BTAC with BA. BVE and BTAC with cetyl alcohol show similar performance at 16% conditioning system [8]. Further research is needed to engineer optimized conditioner formulations based on BVE at consumer relevant use levels.

The present study will examine the effects of fatty alcohol selection and use level on lamellar gel network (LGN) formation and properties when formulating with BVE and provide a comparison to the industry benchmark for conditioning performance, BTAC. Their respective structures, differing mainly in the head group – primary amine esylate and quaternary ammonium chloride, respectively – can impact surfactant packing parameter and self-assembly behavior, also when combined with long chain fatty alcohols. The impact of this key structural difference of cationic amino lipid is examined at the microscopic and macroscopic levels to relate that behavior to observed differences in formulation properties and hair conditioning performance. Formulation properties and conditioning performance are impacted by total concentration of the conditioning system, the ratio of cationic lipid to fatty alcohol, and processing conditions as well as age of the formulation. To allow a meaningful comparison of BVE systems to BTAC systems, we deployed the exact same formulating process for all samples mimicking large scale conditions, and total concentrations and ratios of cationic lipid to fatty alcohols in line with commercial conditioner formulations.

Materials and Methods. BVE was obtained from INOLEX, Inc. (Philadelphia, PA, USA) as AminoSensyl™. Cetyl alcohol and stearyl alcohol were obtained from INOLEX, Inc. (Philadelphia, PA, USA). BTAC was obtained from Clariant Corporation (Louisville, KY, USA) as Genamin® BTLF (70%). Calcium gluconate and the broad-spectrum preservation system Zeastat™ were obtained from INOLEX, Inc. (Philadelphia, PA, USA). Citric acid and sodium chloride were obtained from Sigma-Aldrich Corporation (Saint Louis, MO, USA). Dimethicone was obtained from Dow Chemical Company (Midland, MI, USA) as XIAMETER™ PMX-200 Silicone Fluid 350 cSt. All materials, including the surfactants and fatty alcohols, had been used without further purification. Deionized water was used for all experiments. Formulations were made at an approximate 1:3 ratio of cationic surfactant to fatty alcohol and 8% solids use level of the active conditioning system for all measurements except for x-ray. X-ray analysis was performed on samples with ratios varying from approximately 1:1 to 1:3 and solids use levels of 6% to 16%, all % values are weight/weight.

Table 1. Chassis hair conditioner formulations.

Ingredient (INCI)	BVE + BA Formula Wt%	BVE + CSA Formula Wt%	BTAC + CSA Formula Wt%
Water	Q.S. to 100%	Q.S. to 100%	Q.S. to 100%
Caprylhydroxamic Acid (and) Propanediol	0.5 – 2.0	0.5 – 2.0	0.5 – 2.0
Calcium Gluconate	0.0 – 2.0	0.0 – 2.0	0.0 – 2.0
Brassicyl Valinate Esylate	1.0 – 5.0	1.0 – 5.0	0.0
Behentrimonium Chloride	0.0	0.0	1.0 – 5.0
Brassica Alcohol	5.0 – 15.0	0.0	0.0
Cetearyl Alcohol	0.0	5.0 – 15.0	5.0 – 15.0
Dimethicone (350 cSt)	0.0 – 3.0	0.0 – 3.0	0.0 – 3.0
Water (and) Citric Acid	Q.S. to 4.5	Q.S. to 4.5	Q.S. to 4.5

Total	**100.0**	**100.0**	**100.0**

If not stated otherwise, formulations had been made by a) combining water and the preservation system in an adequate beaker with heating and propeller mixer, heating to 70°C under continued stirring at 350 rpm, b) addition of cationic surfactant and fatty alcohol, sodium chloride, and calcium gluconate, heating to 80°C until fully melted, adding silicone- and other conditioning-oils, stirring for 15 min until homogeneous, heat is removed, c) at 70°C, homogenizing at 3500rpm for 3 minutes with a Silverson L5M-A with a standard 2" head with the six hole emulsor screen, d) stirring with an anchor mixer at 150 rpm until temperature drops to 45°C, addition of final pH-adjuster (citric acid) to adjust pH to 4.0 ± 0.5, and e) transferring to an appropriate container. Cationic surfactants BVE and BTAC are formulated with varying ratios of different fatty alcohols to determine the effects of C-chain length and blend ratio on the LC phase behavior, LGN properties, and hair conditioning performance. Measurements had been performed 7 to 14 days after samples had been prepared.

LC structure and morphology are characterized using polarized light microscopy (PLM), small- and wide-angle X-ray scattering (SWAXS), and rheological analysis is used to quantify macroscopic fluid properties. Hair conditioning performance is assessed on single hair fibers (contact angle) and on hair tresses via instrumental testing on hair tresses (wet/dry combing, static build-up), and by consumer sensory perception during home-use.

Polarized Light Microscopy

PLM images were taken with an Olympus BH-2 equipped with brightfield and polarization microscopy.

Small and Wide Angle X-ray Scattering

SWAXS measurements were performed using a Xeuss 2.0 system (Xenocs SAS, Grenoble, France) using the copper x-ray source (K_a wavelength of $\lambda = 0.1542$ nm), a 1M Pilatus solid state detector for small angle scattering and a 100K Dectris detector for scattering up to 45°, a capillary sample holder at a temperature of 25°C, and a high-resolution collimation setting.

Samples were enclosed in vacuum tight thin soda-glass ("Spezialglas") capillaries with an outer diameter of 1 mm and thickness of 10 µm (WJM-Glas Müller GmbH, Berlin, Germany). Two-dimensional intensity data were transformed to one-dimensional scattering curves as a function of the magnitude of the scattering vector, $q = 4\pi/\lambda \cdot \sin(q/2)$, where q is the scattering angle, with Xenoc's data reduction software (Foxtrot). Ag-behenate was used for q calibration. All data were normalized and corrected for the background scattering from the capillary and solvent.

Rheology

To determine the rheological properties of each sample, testing was performed on a TA Instruments AR-G2 Rheometer at QAT Labs (Peachtree Corners, Georgia). An oscillation strain sweep test was performed to determine the plateau storage modulus and yield stress. A 40 mm 2° cone plate was used, the angular frequency was set to 6.3 rad/s, and the strain percentage was set to a range of 0.01 to 106%. A frequency sweep test at an amplitude of 0.1% (linear regime) from 0.1rad/s to 100rad/s and a steady-state stress sweep from 0.01 to 100s^{-1} were performed with the same geometry as well.

Hair Swatch Preparation

Hair swatches were prepared by TRI Princeton (Princeton, NJ), and were 3.0 g, 8" in length, and 1" wide. European hair, Latam hair, and Asian hair were all used in this study.

To damage the tresses, bleaching was done with 6% hydrogen peroxide at a pH of 10.2. The tresses were left in the bleach for 40 minutes at 40°C. Once done, they were rinsed under a faucet controlled at 1.0 GPM at 40°C.

To treat the tresses, they were washed with 15% SLES and rinsed under a facet controlled to 1.0 GPM and 40°C. The treatments were applied to damp hair at 15% by weight of the tress, approximately 0.15 mL/g. The conditioner treatment is massaged into the hair for 30 seconds, left in for 3 minutes, then subsequently rinsed out for 30 seconds under the same rinsing conditions (1.0 GPM flow rate, 40°C). Untreated controls were prepared by applying 15%

SLES at 10% by weight of the tress, approximately 0.1 mL/g. The SLES was massaged for 30 seconds, then rinsed for 30 seconds (1.0 GPM flow rate, 40°C).

Hair Contact Angle

Measurements of advancing contact angle via Wilhelmy plate were performance at Augustine Scientific (Newbury, OH). Hair treatments were performed by TRI Princeton (Princeton, NJ). Testing was done on single hair fibers attached to a tensiometer, dipped into both water and diiodomethane.

Hair Antistatic

Antistatic measurements are made on a custom-built apparatus made and performed by TRI Princeton (Princeton, NJ). The device measured static buildup of 8 undamaged European hair tresses after brushing, then their respective charge decay over time under 30% RH conditions. Testing for BTAC was performed on a 1:3 chassis of BTAC and BA instead of with CSA as shown in Table 1.

Hair Anti frizz

Anti frizz measurements were performed via image analysis by TRI Princeton (Princeton, NJ). Measurements were performed with 8 tresses of multi-ethnic hair per tested treatment. The tresses were first washed wit SLES, dried, then combed to a max frizz state that was used as a baseline. Once the baseline was recorded, tresses were treated with the conditioners leave in on damp hair. The tresses were dried overnight, then placed in 80% RH and had images taken over 8 hrs.

Wet and Dry Friction Test

Wet combing force is performed immediately after conditioner treatment. Dry combing force is performed the next day after the above treatment is performed. Combing force is performed on 8 tresses per treatment group tested. Tresses equilibrate overnight in controlled temperature and humidity (60% RH).

Consumer Home-Use Test

Consumer testing was performed via single-blind half head testing by 8-16 untrained panelists. Panelists were asked to use the same shampoo, then compare rated conditioners side by side on a scale from 0-10 for wet hair attributes. After drying, dry hair attributes were ranked.

Results.

Polarized Light Microscopy

Aqueous solutions of 8% concentration of BVE with CSA, BVE with BA, and BTAC with CSA at a 1:3 ratio were made. Polarized light microscopy can be used to detect liquid crystalline phases in a solution. The polarizer function only allows light oriented in a specific direction to pass, and a solution is considered birefringent based on its structure that separates waves of light, that recombine on the analyzer for form bright spots. In samples that have lamellar liquid crystal structure, Maltese crosses are typically observed~~.~~

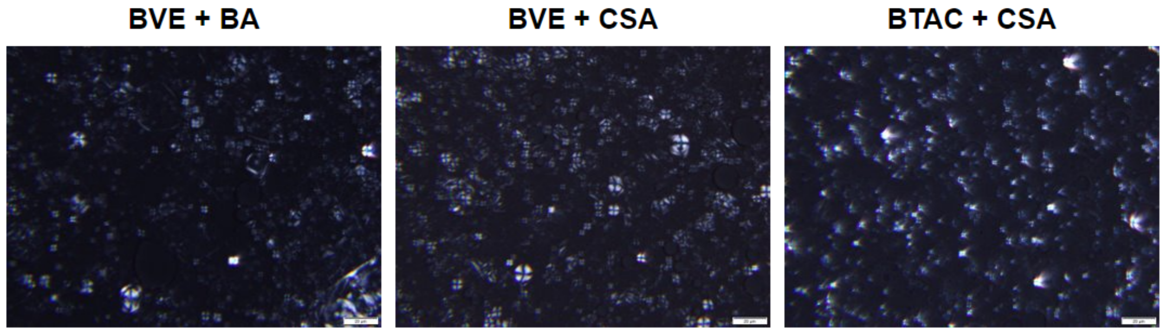

Figure 1. PLM of Chassis Conditioning Formulas.

The three samples exhibit key features of lamellar and/or multilamellar domains: birefringence in the form of Maltese crosses throughout the sample areas.

Small and Wide Angle X-ray Scattering

Figure 2. shows SAXS and WAXS scattering intensity *I(q)* for BVE+BA, BVE+CSA, and BTAC+CSA at 4.3wt%+10.2wt% as examples (top to bottom). The *q*-range below 0.2Å^{-1} shows 3 to 4 distinct peaks. Their respective *q*-values follow the relation 1:2:3:4 indicating a lamellar phase structure. The lamellar spacing is given by $d_{\text{lam}} = 2\pi/q_{001}$ [2]. *I(q)* follows a q^{-2}-dependence expected for lamellar sheets/bilayers in that *q*-range [2]. The wide-angle *q*-range between 1 and 2Å^{-1} shows an intense peak for all samples indicating intra-bilayer

order typical for lamellar α-gel crystals (L_β lamellar phase) [3]. The narrow peak is associated with 2D hexagonal packing of the fatty alcohol and cationic lipid alkyl chains within bilayers. The peak position q_{hex} corresponds to $d_{\mathrm{hex}} = 4.1\pm0.04$Å for all samples (see Figure 3. for a complete sample list). This result shows that the different head groups of BVE and BTAC do not impact the packing density within the bilayers (packing density is one parameter considered relevant for conditioning performance). Peak height scales with bilayer volume fraction Φ of the samples. FWHM peak width is ~50% higher for BVE+BA vs BVE+CSA and BTAC+CSA. This may be an indication of reduced long-range order or some polymorphism for the BA system. BVE+BA has a much narrower overall alkyl chain length distribution compared to BVE+CSA and BTAC+CSA and it is known that more pure lamellar alkyl chain systems tend to form orthorhombic and monoclinic phases in addition to the hexagonal structure [3]. This difference in intra-bilayer structure for BVE+BA may impact its conditioning performance vs the CSA systems. Another parameter impacting macroscopic properties such as rheology and/or conditioning, is the bilayer spacing d_{lam}. For charged bilayers the swelling behavior and therefore d_{lam} depend mainly on bilayer volume fraction, bilayer charge density and ionic strength IS (charge screening and osmotic pressure) [4]. The DLVO theory predicts that d_{lam} is inversely proportional to the screening length κ and thus, proportional to SQRT(1/IS) [4]. Figure 3. shows d_{lam} vs SQRT(1/IS) for samples with different volume fractions, wt-ratios of cationic lipid (BTAC or BVE) to fatty alcohol, added NaCl, and a constant wt-ratio of cationic lipid to Ca-gluconate. Ca-gluconate and NaCl are considered for calculation of IS. Observed values of d_{lam} are between 85 and 240Å, in line with values reported in literature for similar systems at equivalent ionic strengths [4,5,6]. There are no significant differences between BVE+BA, BVE+CSA, BTAC+CSA. For the three systems, ionic strength is the main driver for their swelling behavior. As expected, the observed values for d_{lam} are significantly lower compared to the theoretical maximum $d_{\mathrm{lam,theo}}$ values obtained from only geometric considerations. This indicates that the systems contain excess bulk water and that their rheological properties are driven not only by lamellar domain size, volume fraction and elasticity, but also by inter-domain interaction and network formation of the lamellar domains suspended in bulk water [13]. Overall, we can conclude that BVE + fatty alcohol systems behave fundamentally the same as BTAC and CTAC + fatty alcohol systems – with respect to phase behavior, packing densities, swelling, and response to ionic strength – and can be utilized and processed by formulators in the same way they are used to for CTAC/BTAC. A more detailed analysis of the x-ray scattering behavior including form factor, bilayer elasticity, and dilution behavior will be presented elsewhere.

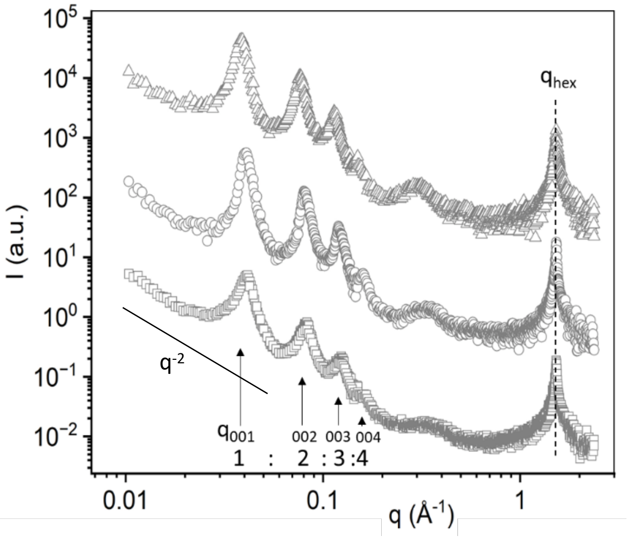

Figure 2. Double-logarithmic plot of SAXS and WAXS scattering intensity I(q) vs magnitude of the scattering vector q for BVE+BA (open triangles △), BVE+CSA (open circles ○), and BTAC+CSA (open squares □), each with 4.3wt% cationic+10.2wt%fatty alcohol (volume fraction Φ = 17.1%). I(q) for BVE+BA was shifted by a factor of 100 and BTAC+CSA by 0.01.

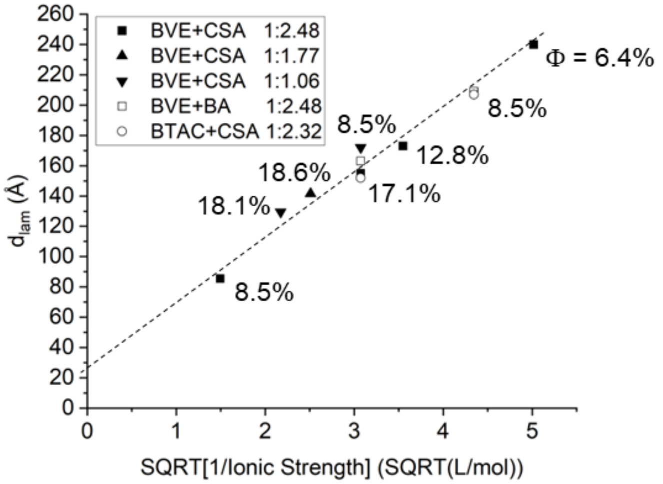

Figure 3. Lamellar spacing d_{lam} from SAXS scattering curves vs SQRT(1/IS) for BVE+BA, BVE+CSA, and BTAC+CSA at varying bilayer volume fraction Φ (see %-numbers in graph), varying wt-ratio cationic lipid to fatty alcohol (see legend),

and a constant wt-ratio of cationic lipid to Ca-gluconate of 1:0.34. The BVE+CSA 1:2.48 sample with Φ = 8.5% and d_{lam} = 84.5Å contains 2 wt% NaCl, all other samples have no added NaCl. The dashed straight line is a guide to the eye.

Rheology

Visco-elastic properties of samples with 8% concentration of BVE with CSA, BVE with BA, and BTAC with CSA at a 1:3 ratio had been measured by oscillatory strain amplitude sweeps, oscillatory frequency sweeps in the linear regime (i.e. below the critical strain γ_c), and viscosity versus shear rate sweeps. The three samples exhibit the typical rheology behavior of lamellar α-gel phases: the viscosity vs shear rate follows a power law with exponents of -0.66 to -0.77 for the three samples for shear rates between 0.01 to 10 rad/s, storage modulus *G'* is 5 to 10 times higher compared to the loss modulus *G''* for the measured frequency range, and the plateau values of *G'* are between 300 and 2000Pa [14]. Yield stress values σ_s are obtained with the crossover method [9] from the amplitude sweep curves using σ_s = *strain*%/100·SQRT($G'^2+G''^2$), with *strain*% and modulus values from the cross-over of *G'* and *G''*, at which *G'* = *G''*. Plateau storage modulus and yield stress are significantly larger for BTAC+CSA vs BVE+CSA and BVE+BA following roughly 4:2:1 for *G'* and 16:4:1 for σ_s (see Table 2.). It is speculated in the literature that higher *G'* and σ_s result in more resistance to dilution and therefore potentially more efficacious conditioning performance. E.g. Iwata et al. have shown for BTMS vs BTAC systems that BTMS has higher values compared to the respective BTAC systems and the BTMS samples also show better reduction in combing force [5].

Table 2. Plateau Storage Modulus G' and Yield Stress from Oscillation strain sweeps of hair conditioner chassis formulas with 8% w/w conditioning system and a ratio of 1:3 for cationic lipid to fatty alcohol.

Treatment	Plateau storage modulus G' (Pa)	Yield Stress (Pa)
BVE + BA	385	3
BVE + CSA	729	13
BTAC + CSA	1481	64

Hair Contact Angle

Healthy hair has a protective hydrophobic fatty outer layer, 18-methyleicosanoic acid (18-MEA), that is attached to the cuticle by a thioester bond. When hair is damaged, either mechanically or chemically, that 18-MEA layer is removed and left behind are hydrophilic sulfonate groups. The resulting hydrophilicity of hair can be used as a measure of damage, via contact angle of water on hair. The greater the damage/hydrophilicity, the lower the contact angle of water on hair as it is easier to wet [1]. LGN conditioners should effectively deposit onto hair and restore hydrophobicity, increasing the contact angle with water. Figure 4 shows the contact angle of water on Asian hair that is damaged and single bleached. Chassis conditioner treatments with dimethicone were applied to the bleached hair tress.

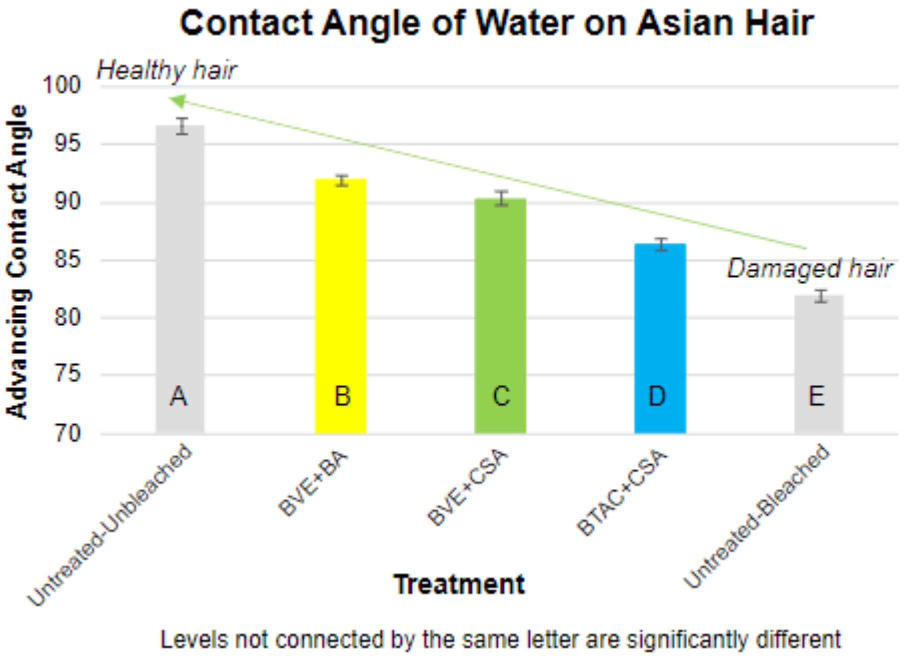

Figure 2. Advancing contact angle of water on Asian hair.

The BVE treatments show a significant improvement in hydrophobicity of the hair surface over the fibers that were untreated and unbleached, showing effective deposition and surface modification.

Hair Antistatic

An effect of conditioner deposition onto hair is to reduce static build-up during combing, especially under low humidity conditions. Human hair ranks highly positive on the triboelectric series, a measure of materials and their tendencies to lose (positive) or gain (negative) electrons easier than others. As a comb passes through hair, electrons are more likely to pass to the comb and cause positive chargers on hair fibers that are highly repulsive. There are a few explanations as to why hair conditioner treatments mitigate this behavior. One being that the deposition of a cationic surfactant facilitates charge dissipation by shifting human hair down to a more neutral point on the triboelectric series. Another theory is that the surface lubrication provided by the deposition reduces friction that reduces charge build-up [15]. The static build up for BVE+BA, BVE+CSA, and BTAC+BA were compared as a percent reduction from an untreated control, where a higher value indicates better performance.

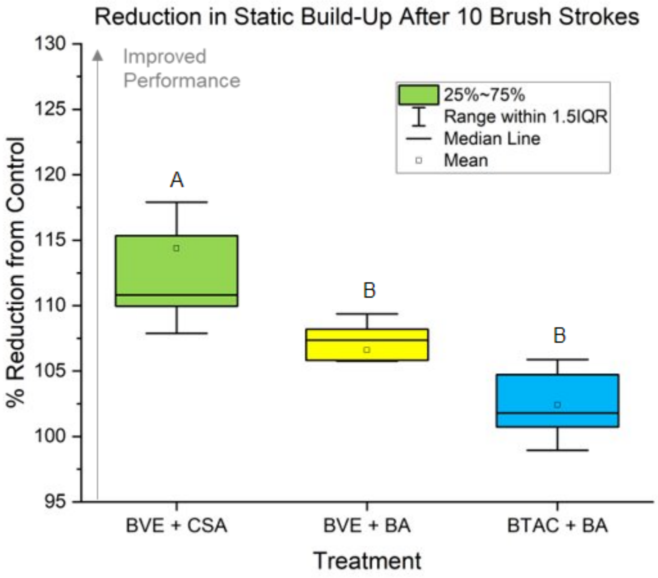

Figure 3. Percent reduction of static build up following 10 brush strokes.

Across all brush strokes measured and the dissipation afterwards, all three treatments showed an effective reduction in static build-up. Figure 5 displays the statistically greater reduction in static build up of BVE+CSA compared to the other treatments.

Hair Anti frizz

According to Mintel, some of the top claims for BTAC conditioners released in the last year had claims related to brightening and illuminating of hair [16]. Anti-frizz is associated with hair that is sleek, smooth, and shiny due to the high alignment of the hair fibers allowing for a “brightened” and “illuminated” appearance. Under high humidity conditions the secondary bonds that structure a hair tress through hydrogen bonding of amino acids solvated by water. This results in frizzy or unruly hair, especially in wavy/curly hair types [10]. Figure 6 shows the percent reduction of frizz state of a multiethnic curly hair tress from its maximum frizz potential, via image analysis and pixel count.

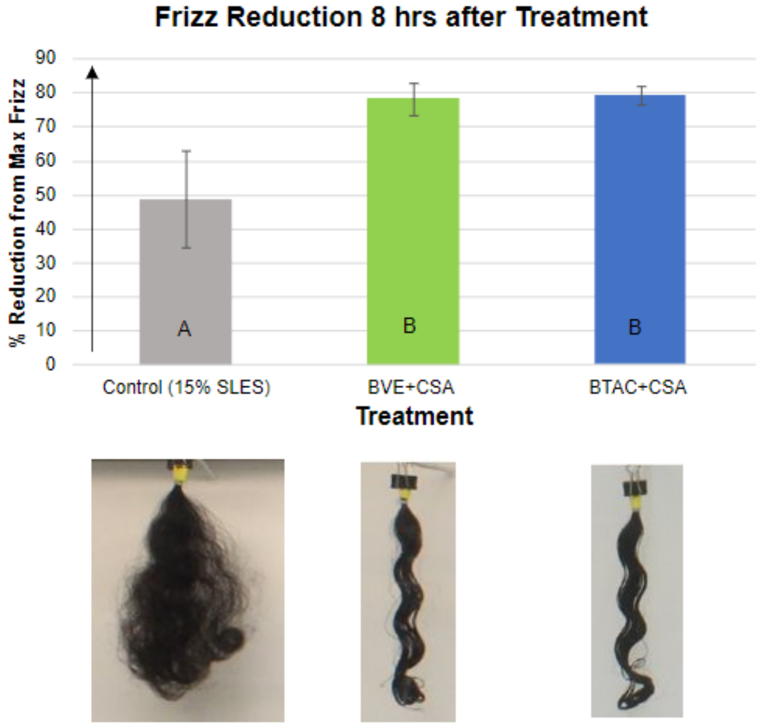

Figure 4. Reduction of frizz from maximum frizz state of curly Latam hair tresses.

Both BVE+CSA and BTAC+CSA as leave-in treatments show significant improvement over a control hair tress only treated with SLES. Results shown are at 8 hours at 80% RH but were consistent across all previous timepoints. The effectiveness is potentially due to the ability of the conditioners to deposit onto the hair and create a hydrophobic layer than inhibiting moisture adsorption.

Wet and Dry Friction Test

Effectiveness of hair conditioners can be quantified by surface lubrication and correlated to consumer desired sensory attributes of moisturization and hydration. Rinse-off conditioners function by depositing LLCs onto the hair to provide surface lubrication that makes hair grooming more manageable. Surface lubrication can be further increased with addition of silicones or ester oils [7]. Chassis rinse off conditioners as presented in figure 7, were tested against an untreated control and each other for their ability to reduce comb force of three different bleached hair types in the wet state.

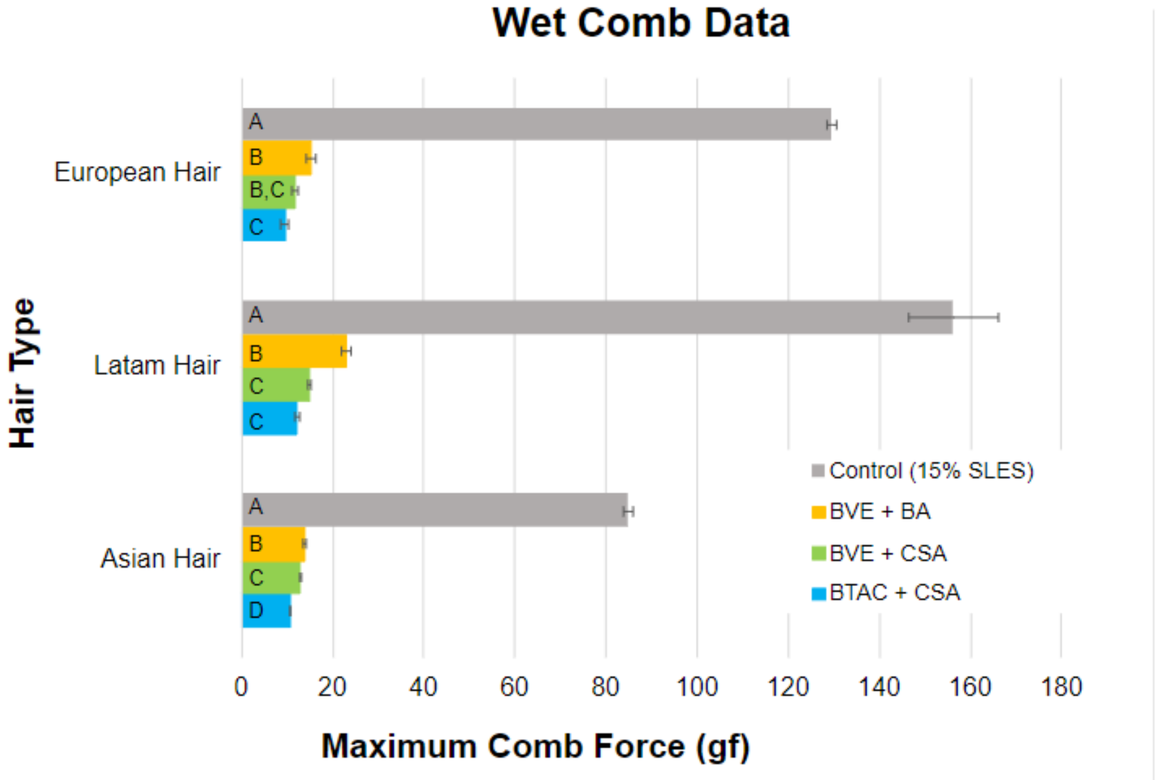

Figure 5. Maximum comb force of treatments on three different hair types.

Across the three different hair types a trend is seen where BVE+CSA shows improved performance over BVE+BA. For European and Latam hair, BVE+CSA shows statistically equivalent performance to BTAC+BA. The comb force results for Asian hair show greater differentiation among the results. This is potentially because Asian hair has a thicker/stronger hair surface than other hair types. This can be seen with the significantly lower comb force value of the control for the Asian hair compared to the other hair types.

Dry combing force (not shown) was also performed on bleached European hair tresses. Results were similar, in that BVE+CSA was equivalent to BTAC+CSA, which were both better than BVE+BA.

Consumer Home-Use Test

Consumer sensory testing bridges the gap between instrumental results and consumer perception and language. The consumer acceptance of the three chassis formulas with dimethicone were tested across panelists of varied hair types: ethnicities, state of damage, age. The rankings from the half head assessment in the wet state are shown in Figure 8.

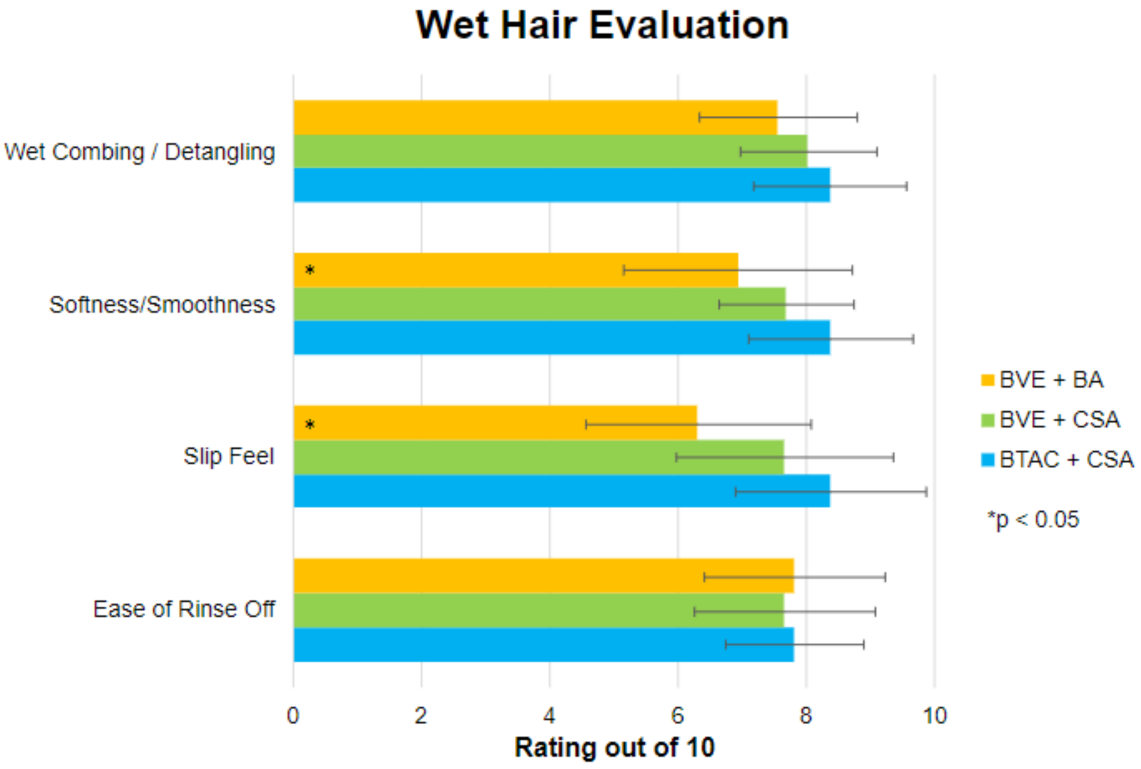

Figure 6. Sensory evaluation of treatments during wet hair application.

The panelists rated the assessed parameters with similar trends across the three different treatments as seen in Figure 8, although most results were significantly equivalent. There were preferences for the BVE+CSA and BTAC+CSA treatments, which only performed statistically better for the perceived softness/smoothness and slip feel. These sensory results correlate to what was seen for the instrumental combing force. Similarly, an assessment on dry hair was performed after this wet hair application. Results are not shown but have the same trends in preference towards BVE+CSA and BTAC+CSA, also correlating to the dry combing force instrumental measurements.

Discussion.

Conditioning performance of hair conditioning systems depends on many different formulation properties, e.g. charge density of bilayers and dilution behavior for substantivity on the anionic hair surfaces, inter- and intra-bilayer friction forces, bilayer elasticity, lamellar domain sizes and interaction, including network formation, all linked to bilayer integrity and macroscopic visco-elastic properties.

General behavior: The PLM and SWAXS data show that all three investigated systems form lamellar gel networks with an intra-bilayer order. The difference in head group between BVE and BTAC does not impact intra-bilayer packing density. Their swelling behavior is dominated by ionic strength as expected for charged bilayers. Macroscopic visco-elastic properties of the samples did show significant differences indicating differences in lamellar domain size and/or interaction, and in network formation. The increasing plateau modulus and yield stress for BVE+BA, BVE+CSA, and BTAC+CSA follow the differences observed in the friction force measurements on treated hair tresses. All three systems, though, do show substantial improvements in conditioning properties of different hair types: increase in hydrophobicity of hair surfaces, reduction of static build up and reduction in wet and dry combing forces.

Impact of fatty alcohol: BVE+BA vs BVE+CSA and BTAC+CSA: BVE+BA exhibits a 5°C higher transition temperature from L_β to L_α (DSC, data not shown) compared to BVE+CSA and BTAC+CSA. Further, the WAXS data show a broader peak for the intra-bilayer order and possibly onsets of additional peaks in that q range for BVE+BA, indicating differences in packing compared to BVE+CSA and BTAC+CSA, with impacts on friction forces and network formation, and therefore on visco-elastic properties and conditioning performance as observed. The broader carbon chain distribution with a shorter average carbon chain length in BVE+CSA and BTAC+CSA leads to improved combing force reduction.

Impact of cationic head group: BVE+CSA vs BTAC+CSA: intra-bilayer packing and lamellar swelling behavior did not show differences in dependence of the head group. Rheology data show a significantly higher plateau storage modulus and yield stress for BTAC+CSA indicating possible differences in bilayer elasticity, domain sizes and network formation between the two systems. However, key conditioning properties did show no or only minor differences for the two systems, which are only statistically significant for wet combing forces on low-damaged Asian hair and had not been perceivable in the sensory half-head evaluation. One resulting question is whether further optimized BVE and CSA systems with increased viscosity, storage modulus, and yield stress, may exhibit further improved conditioning performance.

Conclusion.

Cationic amino lipid conditioning agents, e.g. BVE, can deliver equivalent conditioning performance to traditional quats, e.g. BTAC, while improving upon the sustainability and safety profiles. One principal variable to tune conditioning intensity is varying the C-chain length of the fatty alcohol in the LGN system at Cationic:Falc ratios most relevant to commercial products. Key defining parameters for microscopic and macroscopic properties of BVE+CSA are in general comparable to BTAC/BTMS/CTAC systems investigated here and described in literature.

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References.

[1] Tokunaga S, Tanamachi H, Ishikawa K. Degradation of Hair Surface: Importance of 18-MEA and Epicuticle, Cosmetics 6 (2019) 1-18.

[2] Nallet F., Laversanne R., Roux D., Modelling X-ray or neutron scattering spectra of lyotropic lamellar phases: interplay between form and structure factors, J. Phys. II France 3 (1993) 487-502.

[3] Wunsch K., Relkin P., Cuvelier G., Clément F., Nicolas-Morgantini L., Benkhelifa H., Flick D., Effect of surfactant on structure thermal behavior of cetyl stearyl alcohols, J. Therm. Anal. Calorim. 123 (2016) 1411-1417.

[4] Eccleston, G.M., Behan-Martin, M.K., Jones, G.R., and Towns-Andrews, E., Synchrotron X-ray investigations into the lamellar gel phase formed in pharmaceutical

creams prepared with cetrimide and fatty alcohols, International Journal of Pharmaceutics, 203 (2000) 127-139.

[5] Iwata T., Aramaki K., Effect of the Behenyl Trimethyl Ammonium Counterion on the Lamellar Gel Property, IFSCC Magazine 4 (2013) 249-254.

[6] Gonçalves R.A., Lam Y.-M., Lindman B., Double-Chain Cationic Surfactants: Swelling, Structure, Phase Transitions and Additive Effects, Molecules 26 (2021) 3946-3972.

[7] TA Evans, Evaluating Hair Conditioning with Instrumental Combing. Cosm & Toil 126 (2011) 558-563.

[8] Ajayi O., Davies AR., Amin S. Impact of Processing Conditions on Rheology, Tribology and Wet Lubrication Performance of a Novel Amino Lipid Hair Conditioner. Cosmetics 8 (2021) 1–16.

[9] Davies A.R., Amin S., Microstructure design of CTAC:FA and BTAC:FA lamellar gels for optimized rheological performance utilizing automated formulation platform, International Journal of Cosmetic Science (2020), 1–11.

[10] R. Burgo, Non-petrochemically derived cationic emulsifiers that are neutralized amino acid esters and related compositions and methods, US 8,287,844 B2, 2012.

[11] R. Burgo, Non-petrochemically derived cationic emulsifiers and related compositions and methods, US 20180193233 A1, 2018.

[12] Fevola, M.J. 100% natural and high performance conditioning: The next innovation in amino-acid based cationic ingredients. In-Cosmetics Global; In-Cosmetics: Paris, France, 2019.

[13] Ichihara K., Sugahara T., Akamatsu M., Sakai K., Sakai H., Rheology of α-Gel Formed by Amino Acid-Based Surfactant with Long-Chain Alcohol: Effects of Inorganic Salt Concentration, Langmuir 37 (2021) 7032–7038.

[14] Colafemmina G., Palazzo G., Mateos H., Amin S., Fameau A.L., Olsson U., Gentile L., The cooling process effect on the bilayer phase state of the CTAC/cetearyl alcohol/water surfactant gel, Colloids Surfaces A Physicochem. Eng. Asp. 597 (2020) 124821.

[15] Evans TA, Defining and Controlling Frizz, Cosm & Toil 130 (2015) 46-53.

[16] Mintel GNPD. Search for Behentrimonium Chloride in Hair Care Products. Accessed on 16 May 2022.