JOURNAL OF
CHEMICAL &
ENGINEERING
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Effect of Foam Boosters on Krafft Temperature

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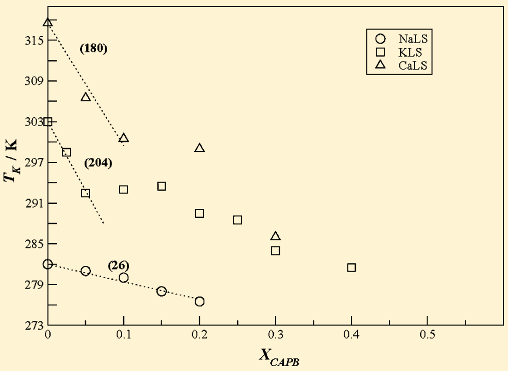
ABSTRACT: The Krafft temperature of three anionic surfactants, that is, sodium lauryl sulfate (NaLS), potassium lauryl sulfate (KLS), and calcium lauryl sulfate (CaLS), have been determined in the presence of foam boosters such as lauric diethanolamide (LDEA), cocoamidopropylbetaine (CAPB), monoethoxylated cocomonoethanolamide (CMEA(EO)$_1$), and cocomonoethanolamide (CMEA). The Krafft temperatures were depressed with the increase in the concentration of the foam boosters. The decrease in Krafft temperature was greater for the surfactant with bivalent counterions compared to the surfactant with monovalent counterions. CAPB was found to be the most efficient among the foam boosters in reducing the Krafft temperature of the surfactants studied.



1. INTRODUCTION

The precipitation of surfactants from aqueous solution is generally undesirable in many surfactant-based product formulations such as detergents. Often surfactants are used in combination with other surfactant or nonsurfactant additives to prevent precipitation. Formulated detergents employ a builder or surfactant mixtures of anionic and nonionic surfactants which permits washing in hard water.

Precipitation of surfactants is also useful in some applications, such as selective plugging of oil reservoirs to improve mobility control and also in recovering surfactants from surfactant-based separation processes. Hence, many surface chemists have noted the importance of the Krafft temperature (T_K) of ionic surfactants and have measured Krafft temperature as well as critical micelle concentrations (cmc's) of many ionic surfactants.[1−5] The Krafft temperature varies significantly with the composition in mixed surfactant systems. The variation in Krafft temperature due to change in counterions, addition of salt, chain length, and mixtures of surfactant have been reported in literature.[6−9] These studies helped in designing the surfactant properties in such a way that they can also be used in hard water.[10,11]

Coconut oil based alkanolamides and betaines are important ingredients of formulation for detergents and personal care formulations although alkanolamides are being increasingly replaced by other components in personal care formulations. These contribute to foam stability in the presence of soil and the antifoaming action of oil droplets in the commercial shampoos and hair conditioners.[12,13] These additives also contribute to the rise in the viscosity of solution and are capable of reducing the irritation action of the surfactant solutions on the eye and the skin.[14]

An approach to study the surfactant precipitation was made by studying the effect of foam booster additives on the Krafft temperature of sodium lauryl sulfate with different counterions. The Krafft temperature was studied by using the conductivity method. In the conductance (κ) versus temperature plot, the temperature at which conductance suddenly rises was taken as the Krafft temperature because the rise in solubility of hydrated surfactant is due to micelle formation which takes place at the Krafft temperature. When the hydrated surfactant becomes soluble (at Krafft temperature) the ions of surfactant are released in solution and hence raise the conductance at that temperature. Thus the temperature when all of the detergent crystals are solubilized should not be treated as the Krafft temperature, but it is the temperature at which a rapid solubility of surfactant in water begins due to micelle formation.[15,16]

In the present article, the effect of various nonionic (alkanolamides) and zwitterionic (betaine) foam boosters on the Krafft temperature is studied. The variation in Krafft temperature of monovalent and bivalent lauryl sulfate surfactants on the addition of foam boosters was also investigated and compared for effectiveness.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. The anionic surfactants used for the study were commercial mixtures of C_{12} to C_{14} surfactants. The average molecular weight values of sodium lauryl sulfate (NaLS) were 0.298 kg·mol^{-1}, potassium lauryl sulfate (KLS) 0.314 kg·mol^{-1}, and calcium lauryl sulfate (CaLS) 0.315 kg·mol^{-1}.

The foam boosters of coconut oil based derivatives cocoamidopropylbetaine (CAPB), cocomonoethanolamide (CMEA), and monoethoxylated cocomonoethanolamide (CMEA(EO)$_1$) were mixtures comprising of C_8 to C_{18} chains. The given average molecular weight of CAPB was 0.360 kg·mol^{-1}, lauric acid diethanolamide (LDEA) 0.301 kg·mol^{-1}, CMEA(EO)$_1$ 0.309 kg·mol^{-1}, and CMEA 0.265 kg·mol^{-1}. All

Received: October 12, 2011
Accepted: January 17, 2012
Published: February 6, 2012

of the above-mentioned surfactants and additives were procured from M/s Galaxy Surfactant Ltd. (India). The CAPB is associated with nearly equimolar strength of NaCl during manufacturing and is mostly used along with this salt in final formulations.[17]

The chemical structures of the four foam boosters (CAPB, LDEA, CMEA(EO)$_1$, CMEA) are shown in Figure 1. Distilled water of conductance 0.0004 S·m^{-1} was used for preparing surfactant solutions for all experimental studies.

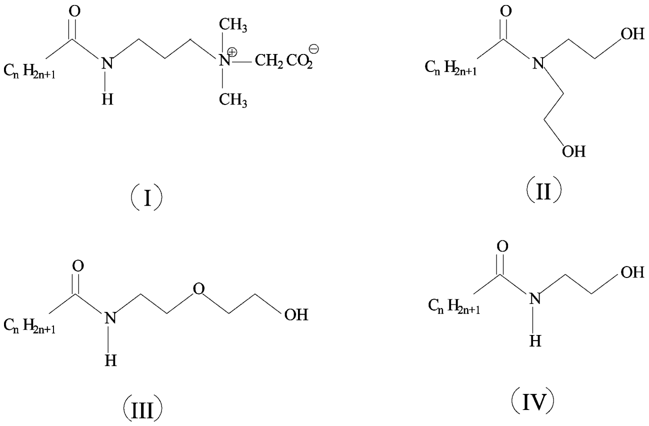


Figure 1. Structures of foam boosters I, cocoamidopropyl betaine; II, lauric acid diethanol amide; III, monooxyethylene cocomonoethanol amide; IV, cocomonoethanol amide.

2.2. Methods and Instrumentation.

Krafft Temperature Measurements. The aqueous solutions prepared were placed at temperature below 273 K for at least 8 h for precipitation. The temperature of the precipitated surfactant system was raised gradually under constant stirring, and its conductance was measured using an auto ranging conductivity meter, TCM 15 (Toshniwal Instruments Pvt. Ltd., India). The Krafft temperature was taken as the temperature where the conductance changes abruptly with temperature.[18] The cell constant of the conductivity cell was 100 m^{-1}. The total concentrations of the solutions were kept constant, and the mole fractions of different surfactants and foam boosters were varied in the solution. All of the experiments were performed at least three times, and the error in the Krafft temperature measurements was approximately ± 0.5 K.

The Krafft temperature (T_K) is the melting point of hydrated solid surfactant.[19] At the Krafft point, the cmc curve crosses over the solubility curve, and micelle formation begins. At that point, the micellar concentration has to increase fast to catch up with the monomer concentration to maintain equilibrium. This requirement leads to an abrupt increase in surfactant solubility in the form of micelles, because the aggregation number is fairly large. Micelles have almost indefinite solubility in water compared to single surfactant molecules which have a limited fairly low solubility, because the hydrophobic part is largely shielded from water contact by polar head groups.[20]

Surface Tension Measurements. The steady state surface tension of single and mixed surfactant solutions were measured using a Krüss K11 tensiometer by the Wilhelmy plate method. The platinum plate used for the measurement had dimensions of 20 × 10 × 0.1 mm (length × height × thickness). The plate was cleaned with distilled water and flamed before each measurement. Each value of surface tension was an average of five readings at intervals of 30 s, and the standard deviation was within 0.5 mN·m^{-1}. All of the experiments were performed at least three times, and the error in the surface tension measurement was approximately 0.2 mN·m^{-1}. The instrument was standardized before each set of measurement by measuring surface tension of water which was 71 ± 1 mN·m^{-1}. All of the measurements were carried out at 303 K using a thermostat that allowed consistent temperature regulation to ± 0.1 K.

The desirable composition of the NaLS–additive mixture was prepared by weighing the known amount of NaLS and varying the amount of additive in the mixture. The addition of additive to NaLS was made in such a way that the total

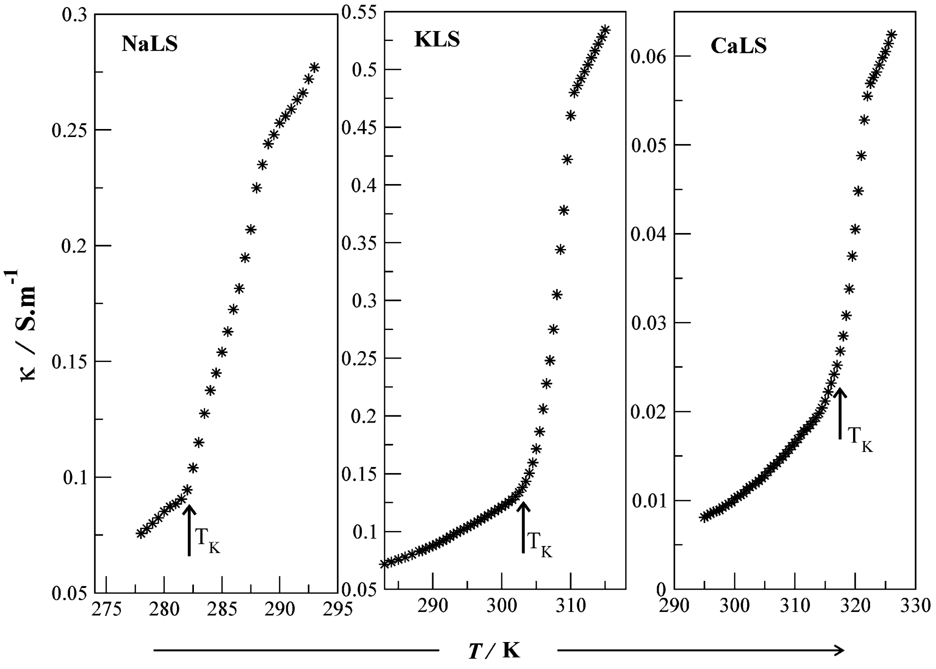


Figure 2. Plot of conductance (κ) against temperature (T) showing the effect of counterions on Krafft temperature (T_K) of lauryl sulfate ions.

surfactant concentration was maintained at 0.1 $\text{mol}\cdot\text{kg}^{-1}$ and mole fraction of additive within the surfactant mixture was varied from 0.1 to 0.9. The cmc was determined as the crossing point of Szyszkowski fit and final surface tension line on the surface tension concentration curve. The errors in cmc values were estimated to be less than 3 %.

3. RESULTS AND DISCUSSION

3.1. Effect of Concentration and Counterion of Surfactant on Krafft Temperature. Anionic surfactants are easily soluble in soft water, but in hard water many of these precipitate out. The precipitation of surfactant can be detrimental in many applications like detergency, oil recovery, and so forth and also can affect formulation composition largely. However, it is also desirable in some cases such as surfactant recovery by crystallization. Additives meant for foam boosting can affect other properties, and Krafft temperature is one of the important properties for any formulation. Thus, the effect of salts on Krafft temperature need to be measured to examine their applicability in hard water. The effect of the counterion has been studied earlier[21] and thus was one of the important parameters for this study.

The conductivity method was used for studying the Krafft temperature of anionic surfactant. The total surfactant concentration used for study was 0.1 $\text{mol}\cdot\text{kg}^{-1}$. The plot of conductance versus temperature graph was used to maintain a sufficient solid phase of surfactant and to have a clear Krafft temperature break. The Krafft temperature of NaLS was found to be 282 ± 0.5 K and changed very little over the range of concentration ((0.02 to 0.1) $\text{mol}\cdot\text{kg}^{-1}$) employed.

Replacing the counterion from Na^+ to K^+ ions changed the Krafft temperature from (282 to 303) K, while replacing it with bivalent Ca^{2+} ions changed the Krafft temperature to 317.5 K as shown in Figure 2. The Krafft temperatures for Na, K, and Ca lauryl sulfate are shown together with hydrated ionic radii and the charge to size ratio in Table 1.

Table 1. Effect of Counterions, Hydrated Radii[27] (r_H), and the Charge to Size Ratio (z') on Krafft Temperature (T_K) of Lauryl Sulfate Ions

	T_K	r_H	z'
counterion	K	nm	nm^{-1}
Na^+	282	0.358	2.8
K^+	303	0.331	3.0
Ca^{2+}	317.5	0.412	4.9

The above observation could be explained as, when the electrolytes are placed in water, they result in ion formation. These ions in aqueous solution are surrounded by water dipoles and exist as hydrated ions. The presence of counterions screens the electrostatic repulsions between the charged headgroups of ionic surfactant. The magnitude of the screening effect depends upon the concentration, charge, and nature of the counterion. Comparing the cations Na^+ and K^+ of the same charges, the smaller the ionic radius of the cation, the greater is its charge density and hence stronger will be its attraction with water molecules.[22] Due to the higher charge density of the cation, the surfactant has weaker ionization, resulting in lower solubility[23] and hence a higher Krafft temperature as shown in Table 1.

In the case of CaLS, the Krafft temperature is higher than NaLS even if the ionic radius of Ca^{2+} is larger than Na^+. However, since Ca^{2+} is a divalent cation, the charge to size ratio (z') or charge density is higher than K^+ and Na^+. Thus the charge to size ratio or charge density of the counterion is seen as a more important parameter affecting the Krafft temperature.

3.2. Effect of Foam Boosters on Krafft Temperature. The activity-based solubility product, that is, K_{sp}, for a monovalent anionic surfactant being precipitated by sodium cation can be written as

$$K_{sp} = [\text{surf}_i]_{\text{mon}}[\text{M}^+]_u \cdot \gamma_i \cdot \gamma_M \tag{1}$$

where $[\text{surf}_i]_{\text{mon}}$ is the monomeric surfactant ion concentration of the precipitating surfactant, $[\text{M}^+]_u$ is the unbound metal ion concentration, and γ_i and γ_M are the activity coefficients of the precipitating surfactant anion and metal cation, respectively.[21] M^+ is the general monovalent metal ion, for example, Na^+ or K^+.

The Krafft temperature is effectively a result of interplay of the increase in solubility with temperature and the change in cmc with temperature. The temperature at which the solubility reaches and goes above the cmc is the Krafft temperature of the surfactant solution. Additives which are foam boosters are not expected to alter the solubility largely but can have a significant effect on the cmc of the surfactant.

The temperature at which the solubility and cmc curves intersect is often called the Krafft temperature. Counterions that can alter the solubility of surfactant by altering its charge density or charge to size ratio (z') will significantly alter the Krafft temperature. Additives which are foam boosters are not expected to alter the solubility largely but can have a significant effect on the cmc of the surfactant. Thus, variation in the cmc will lead to a change in Krafft temperature.

The addition of counterions having a higher charge to size ratio or charge density reduces the ionization of the surfactant, thereby reducing its solubility in the solution and hence an increase in Krafft temperature. Similarly surface active additives reduce the cmc of the surfactant mixture, thus lowering the Krafft temperature of the mixture.

3.2.1. Effect of Foam Boosters on Krafft Temperature of NaLS. The effect of foam booster on Krafft temperature of NaLS was investigated by conductivity method as described in section 2.2. The Krafft temperatures of NaLS and its mixtures with foam boosters were measured at total concentration of 0.1 $\text{mol}\cdot\text{kg}^{-1}$. As the proportion of foam boosters increased, the Krafft temperature decreased from 282 K to almost 273 K as observed in Figure 3. The cmc of mixed NaLS-foam booster surfactant was obtained by the surface tension method described in section 2.2. The substitution of NaLS by foam boosters such as LDEA, CMEA(EO)_1, CMEA (nonionic), and CAPB (zwitterionic) reduces the cmc of NaLS in the order CAPB > LDEA > CMEA(EO)_1 > CMEA as seen in Table 2.

The addition of nonionic foam boosters like LDEA, CMEA(EO)_1, and CMEA lowers the micelle formation concentration of surfactant, and as a result the Krafft temperature of the solution is lowered. The addition of CAPB to NaLS reduces the absolute electric potential on the micelle surface due to the attractive interaction between the NaLS and the CAPB.[24] This favors micellization at lower concentrations (lower cmc), resulting in a lower Krafft temperature for the system.[8] The variation in Krafft temperature of the mixture due to the addition of foam boosters is represented in Figure 3.

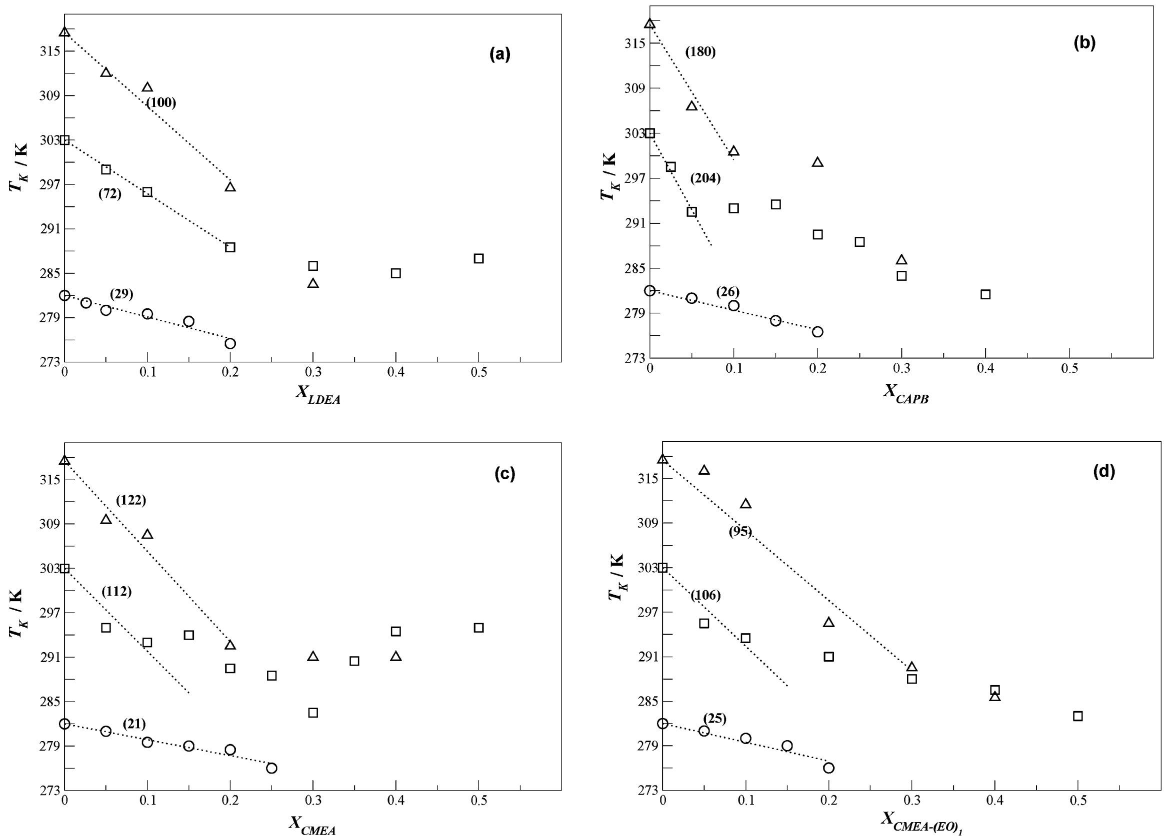


Figure 3. Effect of foam boosters on Krafft temperature (T_K) of different lauryl sulfate counterions at various mole fractions (X). The lauryl sulfate counterions are represented by using symbols ○ for NaLS; □ for KLS; and △ for CaLS. The dotted line shows the initial slope (values shown in brackets), K·mole fraction^{-1}.

Table 2. Critical Micelle Concentration of Foam Booster–NaLS Mixtures as a Function of Mole Fraction (X) of the Foam Booster

	cmc/mol·kg^{-1}·10^3			
X	LDEA	CMEA(EO)$_1$	CMEA	CAPB
NaLS	4.0	4.0	4.0	4.0
0.1	1.0	0.83	0.71	0.35
0.2	0.50	0.44	0.18	0.22
0.3	0.18	0.22	0.17	0.21
0.5	0.11	0.10		0.05
0.7	0.16	0.17		0.06
0.9	0.12			0.04
foam booster	0.08	0.05		0.07

The reciprocal of the slope shown in Figure 3 indicates the proportion of foam booster needed per unit reduction of Krafft temperature. Only 0.034 mole fraction LDEA is required per unit (1 K) reduction in Krafft temperature, while higher proportions of CAPB (0.038 K^{-1}), CMEA (0.048 K^{-1}), and CMEA(EO)$_1$ (0.040 K^{-1}) are required. LDEA was found to reduce the Krafft temperature of NaLS to a greater extent in comparison to other surface active foam boosters studied as seen in Figure 3. In comparison to other foam boosters, LDEA appeared to be the most effective for the Krafft temperature reduction of all of the surface active foam boosters studied, followed by CAPB and CMEA(EO)$_1$. CMEA was found to have the least effect on the Krafft temperature of NaLS compared to other surface active foam boosters studied.

The addition of one ethylene oxide group to CMEA (i.e., in CMEA(EO)$_1$) not only increases the solubility by favoring hydrogen bonding with water but also significantly reduces the Krafft temperature.[25] The presence of two ethylene oxide groups attached to the N- atom in LDEA results in greater affinity for water or hydrophilicity. The addition of LDEA would, therefore, lead to a reinforcement of the water structure through an increased network of intramolecular hydrogen bond interactions. Strengthening of the water structure would lead to increase in the hydrophobic effect favoring the surfactant molecules to micellize at lower concentrations. Thus, the solubility required for micellization will be attained at lower temperatures.

3.2.2. Effect of Foam Boosters on Krafft Temperature of KLS. The variation in Krafft temperature of KLS by addition of various foam boosters was measured. Some of the measurements required initial heating to dissolve the surfactant. Figure 3 shows a decrease in Krafft temperature with an increase in proportion of foam booster in the surfactant mixture. It was observed that the foam booster caused a greater change in Krafft temperature of KLS compared to NaLS. Only 0.0049 mole fraction CAPB is required per unit (1 K) reduction in Krafft temperature, while higher proportions of CMEA (0.0089 K^{-1}), CMEA(EO)$_1$ (0.0094 K^{-1}), and LDEA (0.014 K^{-1}) are required. The Krafft temperature reduction was found in the order CAPB > CMEA > CMEA(EO)$_1$ > LDEA.

However, the observed trend does not remain the same at higher proportions of foam booster. This may be attributed to the striking changes in the properties of mixed surfactant system observed at 1:3 and 3:1 mole ratios due to close packing and chain length compatibility.[26]

3.2.3. Effect of Foam Boosters on Krafft Temperature of CaLS. The Krafft temperature of aqueous CaLS in the presence and absence of foam boosters was investigated. The total concentration of the surfactant solution was maintained constant at 0.05 $\text{mol}\cdot\text{kg}^{-1}$. The solution was prepared by initially heating the solution above Krafft temperature.

The observed variations in Krafft temperature of CaLS are presented in Figure 3. Only 0.0056 mole fraction of CAPB is required per unit (1 K) reduction in Krafft temperature, while higher proportions of CMEA (0.0082 K^{-1}), LDEA (0.010 K^{-1}), and CMEA$(\text{EO})_1$ (0.011 K^{-1}) are required. The order of their effectiveness can be represented as CAPB > CMEA > LDEA > CMEA$(\text{EO})_1$.

The effect of foam booster on Krafft temperature reduction was greater on KLS and CaLS compared to NaLS. CAPB was observed to reduce the Krafft temperature of all three surfactants to below 273 K as shown in Figure 3b. It was also observed that the reduction in Krafft temperature was the highest for CaLS and the least for NaLS. The reduction in Krafft temperature was seen to level off at higher mole fractions of foam boosters.

4. CONCLUSIONS

The effect of foam boosters and counterions on the Krafft temperature of NaLS was studied by the conductivity method. Changing the counterion of lauryl sulfate ion, the Krafft temperature of LS^- increased in the order $\text{Na}^+ < \text{K}^+ < \text{Ca}^{2+}$. This is attributed to increase in the charge density or charge to size ratio of the counterion.

In the case of the NaLS−foam booster system, the effect of foam booster on Krafft temperature was found to be in the order LDEA > CAPB > CMEA$(\text{EO})_1$ > CMEA. The order for KLS Krafft temperature reduction was CAPB > CMEA > CMEA$(\text{EO})_1$ > LDEA.

The order of Krafft temperature reduction of CaLS is CAPB > CMEA > LDEA > CMEA$(\text{EO})_1$. The Krafft temperature reduction levels off at a higher proportion of the foam booster.

CAPB lowered the Krafft temperature of KLS and CaLS to a greater extent in comparison to other foam boosters studied, suggesting its potential applications in hard water.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank M/s Galaxy Surfactants (India) for providing the surfactant and different foam booster samples.

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