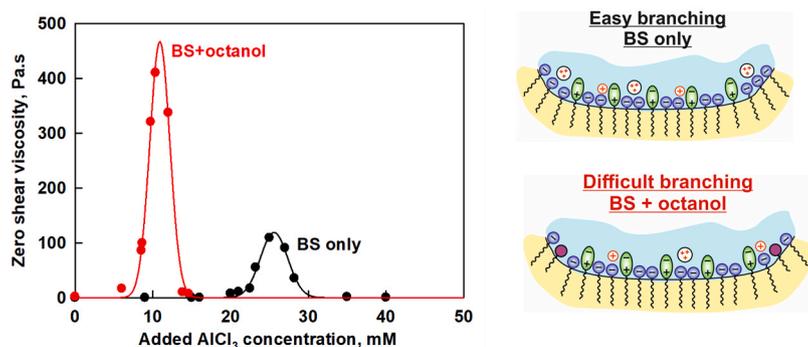


## Interplay between cosurfactants and electrolytes for worm-like micelles formation

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### GRAPHICAL ABSTRACT



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### ABSTRACT

The rheological response of surfactant solutions containing a mixture of anionic and zwitterionic surfactants, in the presence of shorter-chain cationic and nonionic co-surfactants and various counterions was studied experimentally and described theoretically by developing the model that accounts for the competitive adsorption of different monovalent and divalent counterions, as well as the inclusion of co-surfactants within the micelles. This model was used to predict the salt curve dependence of systems with various salt and co-surfactant concentrations and was tested against the experimentally measured salt curves. A good agreement was found between the experimental data and the proposed theoretical model. It was demonstrated that the adsorption energies of counterions on the micellar surfaces remain unchanged with the addition of co-surfactants. However, the conditions for micelle branching are significantly affected, particularly in the presence of divalent and trivalent counterions. The presence of co-surfactants reduces the number of adsorbed divalent ions, thereby diminishing their effect on micelle branching.

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## 1. Introduction

Micellar solutions are widely used in various formulations such as shampoos, body washes, liquid detergents, etc. [1–5]. Their properties can be modified by different factors, such as pH, temperature, and salt concentration, depending on the nature of the surfactant molecules [6]. The effect of electrolytes on ionic surfactants is straightforward, leading to a viscosity peak at intermediate salt concentrations. This is explained as follows: before the peak, the salt screens the electrostatic repulsion between charged surfactant molecules in the micelles, decreasing the average area per molecule, increasing the packing parameter, and leading to the formation of longer (eventually wormlike) micelles [7–9]. At high salt concentrations, there is a decrease in viscosity, which is attributed to the appearance of micelle branching or shortening [10,11]. Wormlike micellar solutions exhibit specific rheological behavior, described as viscoelastic and shear-thinning. These solutions can be characterized by several parameters, such as zero-shear viscosity, plateau modulus, breaking-recombination time and reptation time [12].

In numerous studies the effect of different electrolytes on micellar rheological properties is analyzed. For some of the systems a correlation is found between solution rheological behavior and Hofmeister series [13–20] showing that the ions are more likely to interact with counter ions with similar water affinity (kosmotrope or chaotrope). For example, chaotropes, which are presented as big and “soft”, form smaller hydration shell and could easily lose water molecules forming direct contact pair with another ion with similar hydration shell. Chaotrope (like potassium) shift salt curve for sodium laureth sulfate (SLES) to the left compared to kosmotrope (sodium) leading to viscosity maximum at lower added salt concentration [21–24].

Recently, we demonstrated that substituting part of the ionic surfactant SLES with the zwitterionic surfactant cocoamidopropyl betaine (CAPB) leads to a dramatic increase (more than 20-fold) in the maximum viscosity due to more difficult branching. The presence of CAPB in the solution also alters the interactions between cations and micelle surfaces. Contrary to the expected decrease in maximum viscosity when potassium is used as the counterion, an increase in viscosity was observed compared to the system with sodium. It was shown that the maximum viscosity in the salt curve decreases linearly with the ratio of the counterion's valence to its hydrated radius,  $Z/R$  [24]. Additionally, it was found that the length of the micelles and their branching are governed by the interactions of the counterions with both surfactants (SLES and CAPB), while the peak position is not significantly affected by the presence of CAPB in the mixture after accounting for the ratio of counterion concentration to SLES concentration [24].

The presence of co-surfactants can also significantly impact the rheological properties of surfactant solutions, with diverse behaviors observed depending on the nature of the additive, particularly its logP or hydrophobicity [21–23,25–32]. Hydrophobicity governs the partitioning of the molecule within the micelles: more hydrophilic molecules tend to stay in the palisade layer near the hydrophilic head groups, while more hydrophobic molecules are predominantly located in the hydrophobic core [25–32]. Kamada et al. [25] showed that polar additives shift the viscosity peak to a lower hydrophobic surfactant composition because they partition into the palisade layer. On the other hand, the additives with low polarity could decrease the viscosity peak without shifting the surfactant mixing fraction when they are preferentially located in the core.

In our previous study [30], we showed that there is an optimal chain length and head group for inducing formation of wormlike micelles in a mixed SLES+CAPB system without added electrolyte. The use of C8 additives with a small nonionic or cationic head group induces the formation of elongated micelles. This effect is explained by the mismatch between the different chain lengths of the main surfactant and the co-surfactant molecules, which leads to micellar growth [31].

The combined effect of electrolytes and co-surfactants was studied in several papers [21–23,33–36]. In the work of Tang et al. [35], the effects

of both additives and salt (NaCl) were examined, showing that the highest viscosity is observed with molecules of medium hydrophobicity. Parker et al. [22] demonstrated that the presence of small hydrophobic molecules (such as fragrances) affects the salt curves for SLES systems, leading to a leftward shift in the viscosity peak and a decrease in the viscosity amplitude. The authors determine two types of additives depending on their behavior and effect on salt curve: amphiphilic co-surfactants which stay near micellar interface and shift the viscosity maximum position to the lower salt concentrations and co-solvents (more hydrophilic) which do not shift the salt curves but soften micelle leading to smaller persistence length, lower bending constant and lower viscosity. They further generalized the effects of additives [23] by identifying two additional operative mechanisms: the transformation of giant micelles into microemulsions in the presence of long-chain alkanes, which corresponds to a rightward shift in the salt curve; and the stiffening of the interface by highly non-polar hydrocarbons and short or cyclic alkanes, which leads to an increase in both viscosity and the salt curve amplitude. Evidence for the transition from wormlike micelles (WLM) to microemulsions was shown in the work of McCoy et al. [32] using contrast variation SANS, which demonstrated that more hydrophobic molecules induce such a transition at a given concentration.

Although there are several papers dedicated to the combined effect of co-surfactants and electrolytes [21–23,33–36], this field could be further expanded. For example, it is currently not possible to predict the effect of salt concentration in the presence of varying amounts of co-surfactants, particularly when divalent ions, rather than monovalent ions, are used to screen the electrostatic interactions between surfactant molecules within micelles.

In the current study, we simultaneously analyzed the effect of two C8 co-surfactants—trimethyl-1-octylammonium bromide (C8TAB) and 1-octanol (C8OH)—on the salt curve of the SLES+CAPB mixture in the presence of four different salts: two monovalent (NaCl and NH<sub>4</sub>Cl) and two divalent (MgCl<sub>2</sub> and CaCl<sub>2</sub>). Here we present an extended version of the theoretical model proposed by Pleines et al. [21], which accounts for the competitive adsorption of counterions and the effect of co-surfactants on the average area per molecule on micellar surfaces. A simple expression for predicting the salt curve is proposed and tested against the experimental results obtained at different co-surfactant concentrations, showing very good agreement.

## 2. Materials and methods

### 2.1. Materials

The surfactant system, referred to as BS in the text, is a mixture of sodium laureth sulfate (SLES) and cocoamidopropyl betaine (CAPB) in a 2:1 wt ratio. The SLES (STEOL CS-170, Stepan Co., IL, USA) has a molecular mass of 332.4 g/mol, while the CAPB (Tego Betaine F50, Goldschmidt) has a molecular mass of 342.52 g/mol.

Two different co-surfactants with an octyl chain length but different head groups were added to the main surfactant system: 1-octanol (C8OH) with a molecular mass of 130.2 g/mol and a logP of 2.58 (Honeywell-Riedel de Haën, cat. no. 293245), and trimethyl-1-octylammonium bromide (C8TAB) with a molecular mass of 252.2 g/mol and a logP of –0.87 (Sigma-Aldrich, cat. no. 75091).

The effect of several metal chlorides with different valencies was investigated, including sodium chloride (NaCl), ammonium chloride (NH<sub>4</sub>Cl), magnesium dichloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O) (products of Sigma-Aldrich), and calcium dichloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O) (product of Chem-Lab). The parameters of the studied electrolytes and their cationic molecular characteristics are summarized in Ref. [24]. These electrolytes differ significantly in ion charge density, represented by the charge-to-hydrated radius ratio, as well as in their free energy of hydration [24,37–39].

## 2.2. Sample preparation

An initial concentrated surfactant solution was prepared, containing 15 wt% SLES+CAPB at a 2:1 ratio in deionized water, which was purified using a Milli-Q Organex system (Millipore Inc., USA). This mixture was stirred at room temperature until fully dissolved. Electrolyte stock solutions were also prepared at various salt concentrations, ranging from 0.1 to 2 M, depending on the salt type. The working samples were then prepared by sequentially mixing the co-surfactant, stock surfactant solution, deionized water, and finally, the concentrated salt solution. Solutions containing C8TAB were prepared at room temperature, while those with C8OH were dissolved at 40°C. In all cases, mild stirring was applied until a homogeneous solution was obtained (at least 1 h).

The studied samples contained 10 wt% surfactant, corresponding to a molar concentration  $C_S = 298$  mM, 0.5 wt% additive (equivalent to 38.4 mM C8OH and 19.8 mM C8TAB), and electrolyte concentrations varying in the range of 0–0.6 M. In the model calculations, we used molality concentrations to account for the decreased amount of water in the solution at high salt concentrations. For systems without added background electrolytes, the molality concentrations are 224.5 mmol/kg water for SLES and 108.9 mmol/kg water for CAPB in mixtures without added co-surfactants. In the presence of 0.5 wt% co-surfactants, these concentrations increase to 225.8 mmol/kg water for SLES, 109.6 mmol/kg water for CAPB, 43.2 mmol/kg water for C8OH, and 22.3 mmol/kg water for C8TAB.

A set of experiments was also conducted to study the effect of co-surfactant concentration, testing the model's ability to predict the impact of co-surfactant concentration at different salt levels. Experiments with C8TAB at 1.0 wt% and 1.7 wt% in the presence of various NaCl and MgCl<sub>2</sub> concentrations were performed, as well as with 1 wt% C8OH.

All discussed samples in the text were transparent and homogeneous without indication of phase separation for at least one year after their preparation, when were stored at room temperature.

## 2.3. Rheological properties

Rheological measurements were performed on rotational rheometer Bohlin Gemini (Malvern Instruments, UK) by using cone and plate geometry with two different cone diameters depending on solution viscosity. For low viscous samples with viscosity,  $\eta < 1$  Pa.s, a geometry with 60 mm cone diameter and 2° truncation was used, and for those with viscosity above 1 Pa.s, a cone with 40 mm diameter and 4° truncation angle was used.

The protocol for rheological measurements consists of 5 min thermal equilibration and consecutive logarithmical variation of shear rate in the range of 0.01 s<sup>-1</sup> and 300 s<sup>-1</sup>. The viscosity of each sample was determined by 2 independent measurements and the error was determined to be around 10%. Oscillatory measurements were also performed at frequency sweep regime. The sample was equilibrated for 5 min at the working temperature and then frequency was varied between 0.01 and 10 Hz at 2% deformation, which correspond to the linear region in amplitude sweep experiment.

The rheological measurements were performed at least one day after sample preparation in order to equilibrate at room temperature and the measurement temperature was set to 20 °C.

## 2.4. SAXS measurements

SAXS measurements of the micellar solutions were carried out on an inhouse X-ray scattering system (XEUSS 3.0 SAXS/WAXS System, Xenocs, Sassenage, France) with a CuK $\alpha$  X-ray source ( $\lambda=0.154$  nm, Xeuss 3.0 UHR Dual source Mo/Cu, Xenocs, Sassenage, France) and Eiger2.4 M detector (Dectris Ltd., Baden Deattwil, Switzerland) with slit collimation. The details for the experimental conditions are described in Ref. [24]. For the SAXS data modeling the software SASView was used

(<http://www.sasview.org>).

## 3. Experimental results

### 3.1. Effect of counterions and co-surfactants on salt curves

The experimental data for apparent viscosity as a function of shear rate for BS containing 0.5 wt% of C8OH and 0.5 wt% C8TAB in the presence of different salt concentrations are shown in Fig. S1. One sees that at low salt concentrations, the viscosity remains constant as a function of shear rate. However, at higher salt concentrations, the typical dependence for worm-like micelle-containing solutions is observed: viscosity remains constant at low shear rates and decreases with increasing shear rate above a certain threshold shear rate. A linear dependence between  $\eta$  vs  $\dot{\gamma}^{-1}$  is observed, indicating the formation of interwoven worm-like micelles [40,41].

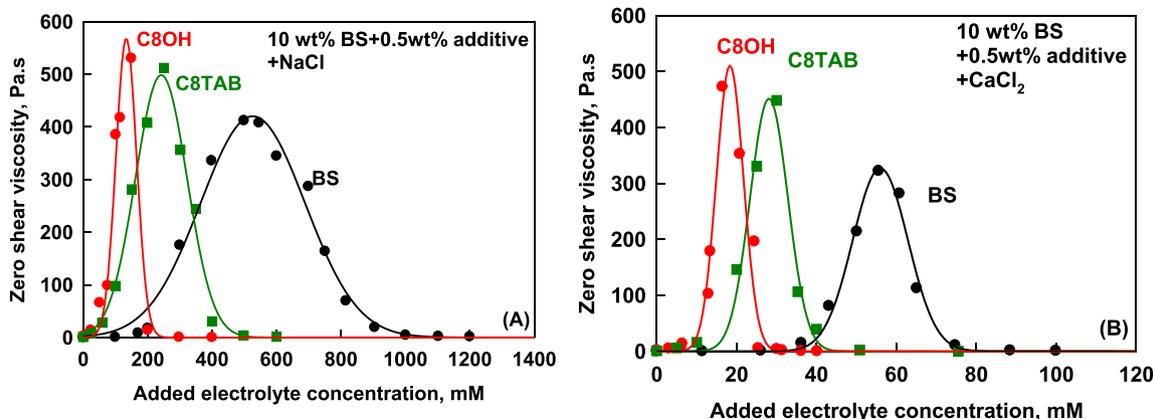
The zero-shear viscosity,  $\eta_0$ , is determined from the measured viscosity at low shear rates before the critical shear rate at which the viscosity starts to decrease, and is plotted as a function of added salt concentration in Fig. S2. It can be seen that for both studied systems (BS+C8TAB and BS+C8OH), the viscosity passes through a maximum as a function of salt concentration. A similar dependence was established in Ref. [24] for BS without co-surfactant. The type of salt used affects the position of the maximum and the maximal viscosity that can be reached. The lowest concentration required to reach the maximal viscosity is observed when Ca<sup>2+</sup> is used as the counterion, followed by Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>.

To compare the effect of added co-surfactants on the salt curves, we replotted the experimental data from Fig. S2 along with results from Ref. [24] in Fig. 1 for a given salt. The obtained curves clearly show that the addition of C8OH decreases the required concentration for reaching the maximal viscosity to a greater extent for all studied salts compared to the effect of C8TAB. Both co-surfactants significantly increase the maximal viscosity for all salts.

To compare the effect of the same counterion on the BS and BS+co-surfactant solutions, we defined three characteristics of the salt curve: maximal viscosity  $\eta_{0MAX}$ , the salt concentration at which this maximal viscosity is reached  $C_{MAX}$ , and the width of the salt curve  $C_\sigma$ . At electrolyte concentrations of  $C_{MAX} \pm C_\sigma$  the viscosity decreases to 60% of  $\eta_{0MAX}$ . The determined characteristics are shown in Table 1.

It can be seen that the presence of 0.5 wt% C8TAB in 10 wt% BS increases  $\eta_{0MAX}$  by 20% for monovalent ions and by 55% for divalent ions. The addition of 0.5 wt% C8OH in 10 wt% BS increases  $\eta_{0MAX}$  by 32% and 65% for monovalent and divalent ions, respectively. The value of  $C_{MAX}$  decreases by a factor of 2 upon the addition of 0.5 wt% C8TAB and by more than a factor of 4 when 0.5 wt% C8OH is added to 10 wt% BS containing monovalent ions. For divalent ions, the decrease in  $C_{MAX}$  is again by a factor of 2 in the presence of 0.5 wt% C8TAB and by a factor of 3 in the presence of 0.5 wt% C8OH.

However, along with the significant reduction in the salt concentration required to induce the maximal viscosity, the concentration range at which the viscosity remains high also decreases significantly upon the addition of co-surfactants. The width of the salt curve decreases by a factor of 2 upon the addition of 0.5 wt% C8TAB for both types of ions, whereas the presence of 0.5 wt% C8OH in the formulation decreases the width by a factor of 5 for monovalent ions and by a factor of 3 for divalent ions. Note that the ratio between the width of the salt curve and the salt concentration required to reach maximal viscosity is almost the same for BS and BS+C8TAB-containing solutions in the presence of monovalent ions and Mg<sup>2+</sup>, and significantly smaller for all Ca<sup>2+</sup>-containing solutions and BS+C8OH formulations. This latter effect indicates easier branching in the presence of Ca<sup>2+</sup> and/or C8OH in the mixture.



**Fig. 1.** Zero shear viscosity as a function of added concentration of (A) NaCl; (B) CaCl<sub>2</sub> for 10 wt% BS (black circles); 10 wt% BS+ 0.5 wt% C8TAB (green squares) and 10 wt% BS +C8OH (red circles).

**Table 1**

Comparison between the viscosity in salt curve maximum, added salt concentration for reaching the maximal viscosity and the peak width.

Characteristics	Co-surfactant	Counterion			
		Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
Viscosity at maximum, $\eta_{MAX}$ , Pa.s	No	420	490	245	326
	C8TAB	500	625	407	460
	C8OH	570	625	425	510
Salt concentration for reaching maximal viscosity, $C_{MAX}$ , mM	No	527	347	88	56
	C8TAB	242	161	42	28
	C8OH	134	87	26	18
Width of salt curve, $C_0$ , mM	No	162	96	22	6.9
	C8TAB	80	47	10	4.7
	C8OH	32	20	5.3	3.4

### 3.2. Effect of counterions and co-surfactants on the mesh size and relaxation times

To characterize the properties of the network formed from interwoven wormlike micelles, the elastic and viscous moduli as a function of oscillation frequency were measured for solutions with different salt concentrations. The obtained experimental data are presented as Cole-Cole plots and shown in Fig. S3 in the Supporting Information (SI). To compare the results obtained with different background electrolytes, we introduce the scaled salt concentration,  $f$ , defined as  $f = \frac{C_{EL} - C_{MAX}}{C_0}$ , where  $C_{EL}$  is the electrolyte concentration in the measured solution, and  $C_{MAX}$  and  $C_0$  are the values given in Table 1 for the respective system.

From the data presented in Fig. S3 in SI, it is seen that the studied samples show viscoelastic behavior, exhibiting Maxwellian relaxation when the scaled concentration  $f$  is between  $-1.5$  and  $+1.5$ . A significant deviation is observed when the electrolyte concentration is outside this range. Such samples resemble living polymers, representing a network of entangled long threads that relax through two parallel processes: reversible scission and reptation [12].

Using the approach of Cates [12], we determined the characteristic parameters of the samples: elasticity at high frequency  $G_0$ , the characteristic time for micelle breaking and reforming  $\tau_{br} = T_R \bar{\zeta}$ , where  $T_R$  is the relaxation time determined from the frequency at which the elastic and viscous moduli are equal to each other, and  $\bar{\zeta}$  is determined from the comparison of numerical plots, calculated by Kern et al. [42], and our experimental data. The mesh size or the mean distance between the micelle segments in the network is calculated from the plateau elasticity using the following expression [43,44]:  $\xi = \left(\frac{kT}{G_0}\right)^{1/3}$ , where  $k$  is Boltzmann constant,  $T$  is temperature.

The obtained characteristics are shown in Fig. S4 as a function of scaled salt concentration,  $f$ . One can see that the elasticity of the samples increases with the increase of  $f$  from  $-2$  to  $1$  and remains almost constant when  $f$  varies between  $1$  and  $2$ . The elasticity is highest (ca. 180 Pa at  $f = 1$ ) for solutions containing C8TAB in the presence of monovalent salts (NaCl and NH<sub>4</sub>Cl) and lowest (ca. 100 Pa at  $f = 1$ ) for solutions containing C<sub>8</sub>OH in the presence of CaCl<sub>2</sub>. All other solutions exhibit intermediate elasticity.

The mesh size of the micellar network decreases as  $f$  increases from  $-2$  to  $0$  and remains almost constant with a value of 30 nm afterwards. The smallest mesh size is determined for C8TAB solutions in the presence of NaCl and NH<sub>4</sub>Cl, while the largest mesh size is observed for C<sub>8</sub>OH in the presence of CaCl<sub>2</sub>, in agreement with the lowest elasticity measured for this system.

The relaxation time passes through a maximum at  $f = 0$  due to a significant increase in the reptation time for these solutions. On the other hand, the breakage time decreases with the increase of  $f$  over the entire salt concentration range, which is in good agreement with results reported in the literature [35,45,46]. Tang et al. [35] attributed the decrease in breakage time with increasing salt concentration to the longer micelle size, which implies more locations at which breakage can occur.

### 3.3. Effect of counterions and co-surfactants on the structure of formed micelles

The micellar structure was determined via small angle X-ray scattering technique (SAXS). The scattering curves for systems with different cosurfactant at varied salt type are shown in Figs. S5 and S6. One can see that in all cases a broad maximum is observed which appears at similar scattering vector. This is characteristic for micellar cross section which is not significantly affected neither by cosurfactant nor by electrolyte. As a consequence, both type of additives induces unidimensional growth of the micelles resulting in WLM formation. There is difference in the initial low- $q$  region which corresponds to bigger micellar dimension but the micellar size is beyond the scope of this technique. The results were evaluated following the approach in Ref. [24] which fit the scattering curves with a core-shell model without accounting for the electrostatic interactions between the molecules which are screened near viscosity maximum. The experimental data from SAXS measurements  $I(q)$  for  $q$  in the range between  $0.03$  and  $0.3 \text{ \AA}^{-1}$  were fitted using the model of infinitely long core-shell cylinders ( $L = 720 \text{ nm}$  was set). The scattering length densities of the solvent and micellar core were set to  $9.44 \times 10^{-6}$  and  $7.32 \times 10^{-6} \text{ \AA}^{-2}$ , respectively, as explained in [24]. The determined parameters are listed in Table S1 where is seen that in all cases the micellar radius is about 3.3 nm or 10 times lower than the mesh size.

This value is similar to that determined for the BS system in presence of electrolytes (without cosurfactant).

#### 4. Theoretical analysis of the obtained experimental results

##### 4.1. Maximal viscosity in the salt curves

In our previous study [24], we showed that replacing part of SLES with CAPB leads to a significant increase in the maximal viscosity without significantly changing the peak position when plotted as a function of the salt/SLES ratio. This increase in viscosity was explained by the more difficult formation of branched micelles when CAPB is present in the micelles due to its higher dipole moment compared to SLES alone.

To calculate the maximal viscosity that can be reached in the presence of different counterions and co-surfactants, we accounted for the higher total surfactant concentration in co-surfactant-containing solutions and the effect of counterions on the conditions for branching. A linear dependence between  $\eta_{MAX}$  and the radius of hydrated ions was established in Ref. [24], while a power-law dependence on the total surfactant concentration was determined, with the power-law index varying between 1 and 2 for interconnected micelles [45,47,48].

The following expression is used in the current study to predict the maximal viscosity in the salt curve:

$$\eta_{MAX} = (A - BR_{ion}^q)m_{tot}^q \quad (1)$$

Where  $\eta_{MAX}$  is the maximal viscosity,  $m_{tot}$  is the total surfactant molality calculated for solutions without added electrolyte, including the molality of dissolved SLES,  $m_{SLES}$ , dissolved CAPB,  $m_{CAPB}$  and molality of added co-surfactant,  $m_{co-surf}$ ,  $R_{ion}$  is the hydrated ionic radius given in Table 1 in Ref. [24]. For the SLES+CAPB mixture at a 2:1 ratio, the  $A$  and  $B$  are determined to be  $1.14 \times 10^4$  and  $2.1 \times 10^4$ , respectively, when  $m_{tot}$  is expressed in [mol/kg water] and  $R_{ion}$  in nm. The value of  $q$  is set to be 2 for solutions without co-surfactants and with co-surfactants in the presence of monovalent salts, and 1.7 for solutions containing co-surfactants and divalent ions. The value of 2 is close to values reported for SLES+CAPB+fatty acids in [45,48], whereas the value of 1.7 is the value predicted for micellar growth in the semi-diluted regime [49,50] and in the unentangled regime [51].

However, as shown in the previous section, the micelles formed in the presence of divalent ions exhibit similar rheological behavior to those formed in the presence of monovalent ions. The change in the value of  $q$  from 2 to 1.7 for co-surfactant-containing solutions in the presence of divalent ions is related to a higher probability of branching in the former case (without co-surfactants). The estimated maximum viscosities, based on Eq. (1), are compared with experimentally determined values in Fig. S7, showing good agreement. Eq. (1) is used to predict the maximum viscosity in salt curves, which is then compared to test the predictions of the theoretical model described below.

##### 4.2. Effect of CAPB on packing parameter of SLES-NaCl containing systems

To predict the salt curve, it is essential to understand how the packing parameter changes with the addition of salt. The model proposed by Pleines et al. [21], which describes the experimental data for SLES with monovalent counterions, assumes that the packing parameter can be calculated using the following expression:

$$p = \frac{v}{(\alpha_1 a_{LES^-} + (1 - \alpha_1) a_{MLES})l} \quad (2)$$

Where  $p$  is packing parameter,  $v$  is the effective molecular volume of SLES, including the hydration water and  $l$  is the mean surfactant length, including the interface thickness, which are assumed to be salt-independent,  $\alpha_1$  is fraction of SLES which is in ionized form,  $a_{LES^-}$  is

area per molecule for ionized LES molecules which is proposed to be  $1 \text{ nm}^2$  [52] and  $a_{MLES}$  is the area per molecule of nonionized MLES which is assumed to be the same independently of the counterion and determined to be  $0.4 \text{ nm}^2$  [21]. It was shown that the values of molecule volume and surfactant chain length correspond to  $v = 0.577 \text{ nm}^3$  and  $l = 2.1 \text{ nm}$  for SLES, respectively [21]. For calculation of  $\alpha_1$  the equilibrium between ionized and non-ionized molecules is assumed and following expression is proposed in Ref. [21].

$$m_{NaLES} = \frac{m_{Na,tot} + m_{SLES,tot} + K_d - \sqrt{(m_{Na,tot} + m_{SLES,tot} + K_d)^2 - 4m_{Na,tot}m_{SLES,tot}}}{2} \quad (3)$$

$$\alpha_1 = \frac{m_{LES^-}}{m_{SLES,tot}} \quad (4)$$

$$K_{d,NaLES} = \frac{m_{Na^+} m_{LES^-}}{m_{NaLES}} \quad (5)$$

Where  $m_{NaLES}$  is the molality of neutralized SLES molecules,  $m_{Na^+}$  is the molality of free  $\text{Na}^+$  which are not bounded to SLES,  $m_{Na,tot}$  is the total molality of Na in the solution and  $m_{SLES,tot}$  is the total molality concentration of SLES. For SLES+NaCl system  $m_{Na,tot}$  is a sum of  $m_{NaCl}$  and  $m_{SLES,tot}$ ,  $K_d$  is the dissociation constant which was found to be 0.26 M for Na-LES [21]. Note that in original work of Pleines et al. [21] the expressions are given as molar concentration, but we prefer to work with molality concentration in order to account for decreased amount of available water in the solutions upon increasing the salt concentration and addition of different components.

To apply the proposed approach for SLES [21] to our mixtures, we first need to account for the presence of CAPB in the solution. To incorporate the effect of CAPB on the packing parameter, we assume that SLES and CAPB form mixed micelles where part of the micelle surface is covered by CAPB molecules. This leads to the following expression for the area per molecule:

$$a = ((1 - \alpha_1)a_{NaLES} + \alpha_1 a_{LES^-})x_{SLES,tot} + a_{CAPB}x_{CAPB,tot} \quad (6)$$

Where  $x_{SLES,tot}$  is fraction of SLES in SLES+CAPB mixture and  $x_{CAPB,tot}$  is the fraction of CAPB. For systems without co-surfactants  $x_{SLES,tot} = 0.66$  and  $x_{CAPB,tot} = 0.33$ . However, for co-surfactant containing systems these values decrease depending on the co-surfactant concentration. For calculations we used  $a_{CAPB} = 0.46 \text{ nm}^2$ . The value of  $\alpha_1$  is calculated by Eq. (4) after accounting that 1 mol CAPB contains 1.12 mol NaCl [24]. The scaled viscosity  $\eta_0/\eta_{0MAX}$  as a function of calculated packing parameter for SLES and SLES+CAPB mixture in presence of NaCl is shown in Fig. 2 below.

##### 4.3. Mixture of monovalent salts for BS (no co-surfactants)

In our previous study we showed that the addition of KCl or  $\text{NH}_4\text{Cl}$  instead of NaCl leads to significant change in the rheological response of BS solution, see Fig. 1 in Ref. [24]. If we directly apply the expressions proposed in Pleines et al. [21] for monovalent counterions we were unable to describe our experimental results even after accounting for the presence of CAPB in the mixture. This is because in the model proposed by Pleines et al., the competition between  $\text{Na}^+$  and other monovalent ions added as a background electrolyte was neglected.

This assumption was reasonable for SLES alone, as very high salt concentrations are required for micellar growth. However, when 33 % of SLES is replaced with CAPB, the required salt concentration for micellar growth is significantly reduced. Additionally, CAPB itself contains 1.12 mol NaCl for each mol of CAPB, meaning that the starting molality of  $\text{Na}^+$  in our system is 0.35 mol/kg. This molality is very close to the molality of  $\text{K}^+$  and  $\text{NH}_4^+$  required to reach the maximal viscosity in the salt curve, which are 0.35 mol/kg and 0.40 mol/kg, respectively.

Thus, the presence of CAPB and its associated  $\text{Na}^+$  contribute to the

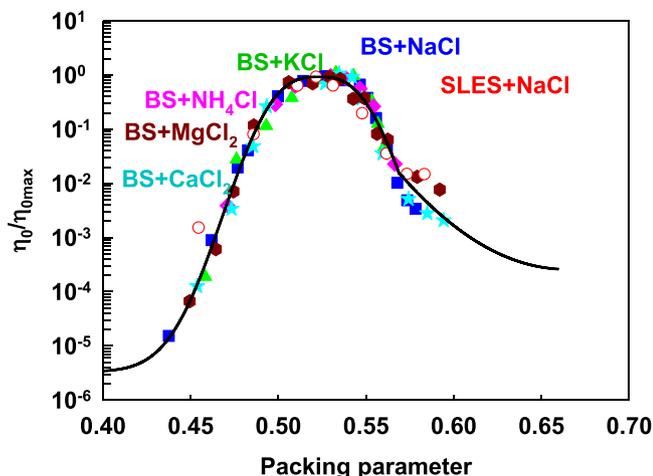


Fig. 2. Scaled zero shear viscosity as a function of packing parameter for BS solutions at different NaCl (blue squares); BS+KCl (red triangles); BS+NH<sub>4</sub>Cl (pink diamonds); BS+MgCl<sub>2</sub> (dark red hexagons); BS+CaCl<sub>2</sub> (cyan stars); SLES+NaCl (red empty circles). The continuous curve is plotted in accordance to Eq. (12).

total Na<sup>+</sup> concentration, makes it comparable to the concentrations of K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> in the system for the lower salt concentrations. This means that the competition between different monovalent ions cannot be neglected, and the model needs to be adjusted to account for these interactions to accurately predict the rheological behavior of the micellar solutions.

To account for the competition between different monovalent ions, we calculate the degree of ionized molecules using the following expression:

$$\alpha_1 = 1 - \frac{m_{\text{NaLES}} + m_{\text{MLES}}}{m_{\text{SLES,tot}}} \quad (7)$$

Where  $m_{\text{MLES}}$  is molality of neutralized LES molecules by K<sup>+</sup> or by NH<sub>4</sub><sup>+</sup> and  $m_{\text{NaLES}}$  is the molality of neutralized LES molecules by Na<sup>+</sup>. For determination of  $m_{\text{NaLES}}$  and  $m_{\text{MLES}}$  the following system of two equations is solved:

$$K_{d,\text{NaLES}} = \frac{(m_{\text{Na}^+,\text{tot}} - m_{\text{NaLES}})(m_{\text{SLES,tot}} - m_{\text{NaLES}} - m_{\text{MLES}})}{m_{\text{NaLES}}} \quad (8)$$

$$K_{d,\text{MLES}} = \frac{(m_{\text{M}^{2+},\text{tot}} - m_{\text{MLES}})(m_{\text{SLES,tot}} - m_{\text{NaLES}} - m_{\text{MLES}})}{m_{\text{MLES}}}$$

Where  $m_{\text{M}^{2+},\text{tot}}$  is molality of KCl or NH<sub>4</sub>Cl, respectively and  $K_{d,\text{MLES}}$  is their dissociation constant. By solving Eq. (8) we determined the values of  $m_{\text{NaLES}}$  and  $m_{\text{MLES}}$ , which are used to determine  $\alpha_1$  from Eq. (7). The area per molecule for KLES and NH<sub>4</sub>LES is assumed to be 0.372 nm<sup>2</sup>, which is related to smaller radius of hydrated ions of K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> than that of Na<sup>+</sup> [24]. The determined dissociation constant for  $K_{d,\text{KLES}} = 0.14$  mol/kg is very close to one determined for by Pleines et al. [21] of 0.11 M. The value of  $K_{d,\text{NH}_4\text{LES}} = 0.182$  mol/kg is slightly higher showing that the ammonium ion is less tightly bound to LES<sup>-</sup> molecules. The scaled viscosity as a function of the packing parameter for BS solutions containing varying concentrations of NaCl, KCl and NH<sub>4</sub>Cl is shown in Fig. 2.

#### 4.3.1. Addition of divalent ions to BS formulation

In our previous study we showed that the addition of MgCl<sub>2</sub> or CaCl<sub>2</sub> instead of NaCl leads to significant decrease in the background electrolyte required for reaching the maximal viscosity, see Fig. 1 in Ref. [24]. In the current study we analysed these results by accounting for competition between divalent ions and monovalent ions and for the fact that one divalent ion is able to neutralize two LES<sup>-</sup> molecules. Therefore, the following expressions are used to calculate the fraction of

ionized LES<sup>-</sup> molecules:

$$\alpha_1 = 1 - \frac{m_{\text{NaLES}} + 2m_{\text{M(LES)}_2}}{m_{\text{SLES,tot}}} \quad (9)$$

Where  $m_{\text{M(LES)}_2}$  is molality of neutralized LES molecules by Mg<sup>2+</sup> or by Ca<sup>2+</sup>. For determination of  $m_{\text{NaLES}}$  and  $m_{\text{M(LES)}_2}$  the following system of two equations is solved:

$$K_{d,\text{NaLES}} = \frac{(m_{\text{Na}^+,\text{tot}} - m_{\text{NaLES}})(m_{\text{SLES,tot}} - m_{\text{NaLES}} - 2m_{\text{M(LES)}_2})}{m_{\text{NaLES}}} \quad (10)$$

$$K_{d,\text{M(LES)}_2} = \frac{(m_{\text{M}^{2+},\text{tot}} - m_{\text{M(LES)}_2})(m_{\text{SLES,tot}} - m_{\text{NaLES}} - 2m_{\text{M(LES)}_2})^2}{m_{\text{NaLES}}}$$

Where  $m_{\text{M}^{2+},\text{tot}}$  is molality of MgCl<sub>2</sub> or CaCl<sub>2</sub> and  $K_{d,\text{M(LES)}_2}$  is their dissociation constant. By using  $K_{d,\text{Mg(LES)}_2} = 0.0062$  mol<sup>2</sup>/kg<sup>2</sup> for Mg(LES)<sub>2</sub> and for  $K_{d,\text{Ca(LES)}_2} = 0.0025$  mol<sup>2</sup>/kg<sup>2</sup> for Ca(LES)<sub>2</sub> we obtained very good agreement between results obtained by different salts before the maximum, Fig. S8 in SI. In contrast, the curves do not follow same dependence after the maximum  $p = 0.5$ . This deviation after the maximum is most probably related to the fact that we assumed that the area per molecule of LES neutralized as M(LES)<sub>2</sub> is the same as it is neutralized as M-LES by monovalent ions. It is well known from the literature that the area per molecule in presence of Mg<sup>2+</sup> is much smaller as compared to the area per molecule in presence of Na<sup>+</sup> [53]. In the initial region when the fraction of M(LES)<sub>2</sub> is relatively small this assumption is justified, but when the fraction of ionized LES molecules become smaller than the fraction of M(LES)<sub>2</sub> the area per molecule is expected to decrease from 0.40 nm<sup>2</sup> down to 0.32 nm<sup>2</sup> for Mg<sup>2+</sup> and down to 0.28 nm<sup>2</sup> for Ca<sup>2+</sup> due to stronger binding of Mg<sup>2+</sup> and Ca<sup>2+</sup> to the micelle surface upon micellar growth [54]. Note that such decrease is reported for LAS molecules [53] and for SDS [55]. That is why we modify Eq. (7) to account for this decrease by using following expression:

$$a = (\alpha_2 a_{\text{M(LES)}_2} + (1 - \alpha_1 - \alpha_2) a_{\text{NaLES}} + \alpha_1 a_{\text{LES}^-}) x_{\text{SLES,tot}} + a_{\text{CAPB}} x_{\text{CAPB,tot}} \quad (11)$$

Where  $\alpha_2 = \frac{2m_{\text{M(LES)}_2}}{m_{\text{SLES,tot}}}$  is the fractions of LES molecules neutralized by divalent ion.  $a_{\text{M(LES)}_2}$  is assumed to be equal to  $a_{\text{MLES}} = 0.4$  nm<sup>2</sup> at  $\alpha_2 < \alpha_1/2$  when divalent ions cannot pack well the molecules that they neutralize and it decreases down to 0.32 nm<sup>2</sup> for Mg<sup>2+</sup> and 0.28 nm<sup>2</sup> for Ca<sup>2+</sup> at  $\alpha_2 > \alpha_1/2$ . Note that the value of 0.28 nm<sup>2</sup> is cross-sectional area for a hydrated sulfate ion [56,57]. Note that according to analysis presented in Ref. [54] the calcium ion is preferentially attached to cylindrical part of the micelles. This means that until there are sufficient number of ionized molecules the attachment of divalent molecules to the surfactant micelle will neutralize two molecules without being able to decrease their area per molecule because other ionized molecules will attract it. Afterwards, the reduction by 12.5 % is observed for Mg<sup>2+</sup> and 30 % by Ca<sup>2+</sup>. Also the smaller area per molecule for Ca<sup>2+</sup> is in good agreement with numerical simulations where we showed that Ca<sup>2+</sup> is strongly attracted to the sulfate group as compared to Mg<sup>2+</sup> [58]. The scaled viscosity as a function of packing parameter is shown in Fig. 2.

The obtained results are plotted as  $\ln(\eta_0/\eta_{0\text{MAX}})$  vs packing parameter. The experimental points are fitted with modified log-normal distribution and the following expression is obtained:

$$\ln(\eta_0/\eta_{0\text{MAX}}) = y_0 + b \exp\left(-\frac{1}{2}\left(\frac{p-p_{\text{max}}}{\sigma}\right)^{k_1}\right) \quad p < 0.57 \quad (12)$$

$$\ln(\eta_0/\eta_{0\text{MAX}}) = B_1 p^2 + B_2 p + B_0 \quad p > 0.57$$

From the best fit we determined the parameters to be  $y_0 = -12.61$ ,  $b = 12.53$ ,  $p_{\text{max}} = 0.5229$ ,  $\sigma = 0.05004$ ;  $k_1 = 2.756$ ;  $B_1 = 451.43$ ,  $B_2 = -599.67$ ,  $B_3 = 190.89$ , showing that the maximal viscosity is reached when packing parameter becomes 0.523. Eq. (12) can be used to predict the flow curves for solutions with different salt concentrations.

#### 4.3.2. Effect of C8TAB concentration on rheological response of BS mixture at different salt concentrations of monovalent ions

From data shown in Fig. 1 above one sees that the presence of 0.5 wt % C8TAB in BS solution leads to significant decrease in the amount of necessary NaCl for reaching the maximal viscosity, which is related to partial neutralization of the SLES molecules by C8TAB molecules which are incorporated in the surfactant micelles. To account for neutralization of SLES molecules by C8TAB we modified Eq. (7) to become:

$$\alpha_1 = 1 - \frac{m_{NaLES} + m_{MLES} + m_{C8TAB}}{m_{SLES,tot}} \quad (13)$$

where  $m_{C8TAB}$  is molality of added C8TAB in the solution. To check the validity of proposed model we calculated the viscosity as a function of added electrolyte concentrations and in presence of different C8TAB concentrations. The obtained experimental data along with the predicted viscosities are compared in Fig. 3 and S9. It is seen that the increase of C8TAB concentration decreases further the salt concentration required to reach the maximal viscosity in salt curves as predicted by Eq. (13). Relatively good agreement between experimentally measured and theoretically predicted viscosities is determined for all studied C8TAB concentrations at various counterions. One sees that the proposed model described very well the experimental data for three studied concentrations of C8TAB (0.5, 1 and 1.7 wt%).

#### 4.3.3. Effect of C8OH on rheological response of BS mixture

The addition of C8OH also affects the salt curve as can be seen from data presented in Fig. 1 above. However, C8OH is nonionic molecule and it cannot neutralize SLES molecules. In our previous study we showed that C8OH is inserted between SLES and CAPB molecules by decreasing the area per molecule within the adsorption layer and forming condense layer on the bubble surface [59]. Therefore, we could expect that C8OH is inserted between SLES and CAPB molecules in the micelles as well. To account for this, we modify Eq. (6) to become:

$$a = (\alpha_1 a_{LES^-} + (1 - \alpha_1) a_{NaLES}) x_{SLES} + a_{CAPB} x_{CAPB} + a_{C8OH} x_{C8OH} \quad (14)$$

$$x_{SLES} = \frac{m_{SLES}}{m_{SLES} + m_{CAPB} + m_{C8OH}}; \quad x_{CAPB} = \frac{m_{CAPB}}{m_{SLES} + m_{CAPB} + m_{C8OH}}; \quad x_{C8OH} = \frac{m_{C8OH}}{m_{SLES} + m_{CAPB} + m_{C8OH}}$$

Where  $m_{C8OH}$  is C8OH molality,  $a_{C8OH}$  is the area per molecule of C8OH on the micelle surface. Assuming that  $a_{C8OH} = 0.25 \text{ nm}^2$  [57,60] we calculated the viscosity as a function of NaCl concentration for 10 wt% BS + 0.5 wt% C8OH, see Fig. S10. The theoretical model predicts reasonably well the data before maximum but overestimate the viscosity after the maximum. There are several possible explanations for this discrepancy between experimental results and theoretical predictions: (1) the type of aggregates formed after the maximum are not branched micelles but discoidal micelles as was shown by Anachkov et al. [48] for SLES+CAPB in presence of C12Ac. However, the measured viscosity curves do not support this hypothesis, see data in Fig. S1, where the slope after the plateau region is equal to  $\dot{\gamma}^{-1}$  which shows that indeed branched micelles are formed but not the discoidal; (2) The area per molecule of ionized molecules decreases due to incorporation of C8OH between them and  $a_{LES^-}$  decreases with the increase of  $x_{C8OH}$ . Note that the similar decrease in area per molecule is well documented for different ionic surfactants containing nonionic admixtures [57,61,62]. It is known that ad-mixtures affects in larger extend the slope of surface tension isotherm in presence of background electrolyte than for solutions without background electrolyte [63] showing that the mean area per molecule decreases in larger extend for solutions containing background electrolyte. The presence of C8OH in the solution is able to change the area per molecule on the solution interface. Most probably when  $x_{LES^-}/x_{C8OH}$  decreases, the formation of H-bonds between sulfate group and hydroxyl group of C8OH is possible [64], because at that stage MLES and CAPB formed also dimers. As a consequence, the mean area decreases significantly at that stage. To account for this effect, we propose the following expression:

$$a_{LES^-} = 1 \quad \text{nm}^2 \quad x_{LES^-}/x_{C8OH} > 2.4$$

$$a_{LES^-} = 205 x_{LES^-} / x_{C8OH}^{0.25} \text{ nm}^2 \quad x_{LES^-}/x_{C8OH} < 2.4 \quad (15)$$

The above equation predicts that at  $x_{LES^-} = x_{C8OH} = 0.5$  the  $a_{LES^-}$  will decrease down to  $0.59 \text{ nm}^2$ . To check the validity of proposed

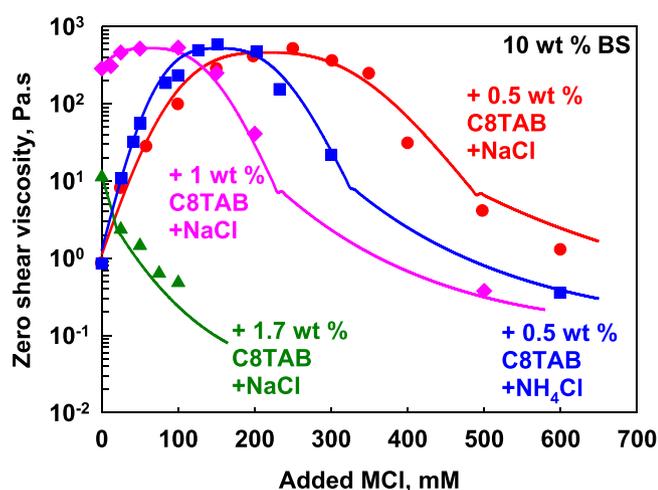


Fig. 3. Zero shear viscosity as a function of NaCl and  $\text{NH}_4\text{Cl}$  concentrations at different C8TAB concentrations. The points represent the experimental results, whereas the curves are plotted in accordance to the described theoretical model.

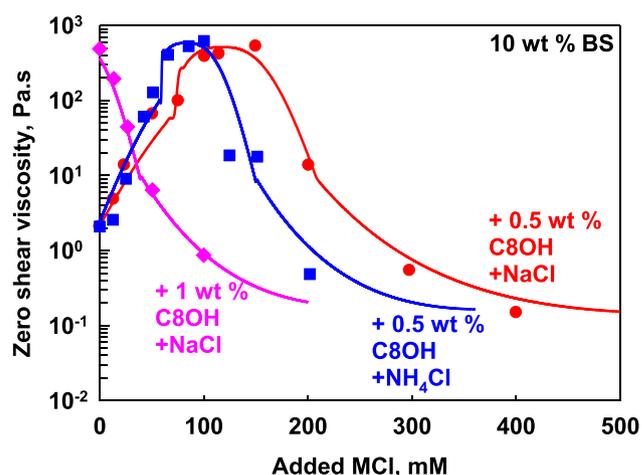


Fig. 4. Zero shear viscosity as a function of NaCl and  $\text{NH}_4\text{Cl}$  concentrations at different C8OH concentrations. The points represent the experimental results, whereas the curves are plotted in accordance to the described theoretical model.

expression the experiments at 1 wt% C8OH were also performed. The description of experimental data with proposed model is shown in Fig. 4 and S11.

## 5. Discussion

### 5.1. Dissociation constants and their relation to adsorption constants of counterions on the adsorption layer

The dissociation constants determined in the current study for BS in the presence of various salt solutions, are shown in Table 2.

The reciprocal value of the dissociation constant corresponds to the adsorption constant, which characterizes the equilibrium between free ions in the solution and ions adsorbed on the micellar surface. The adsorption constant increases with the size of the hydrated ion and its valency. It is known that the adsorption of counterions can be described as [65]:

$$K_{ads} = \frac{1}{K_d} = N_A \delta a_{min} \exp\left(\frac{\Delta\mu^0}{k_B T}\right) \quad (16)$$

Where  $\delta$  is the thickness of the Stern layer, which is expected to be close to the diameter of the hydrated counterion [65] and  $\Delta\mu^0$  is the standard free energy of adsorption (binding) of a counterion from solution to adsorption layer [65] and  $a_{min}$  is the minimal area per molecule neutralized with a given counterions,  $N_A$  is Avogadro number. The obtained values for adsorption of counterions on the micellar surface are in relatively good agreement with results reported in the literature for adsorption of those counterions on the sulfate and sulfonate surfactants layer. Excellent agreement between adsorption energy of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  determined in the current study and the values estimated from molecular dynamic simulation of SLES adsorption layer is established: 3.11 vs 3.24  $k_B T$  for  $\text{Na}^+$  and 4.96 vs 4.62  $k_B T$  for  $\text{Ca}^{2+}$  [58]. The value of 1.68  $k_B T$  reported for  $\text{Na}^+$  adsorption on SDS in [65], is slightly lower compared to value determined in the current study. This is probably related to the fact that the ionic strength of our solutions is very high and activity coefficient of  $\text{Na}^+$  is lower than 1. As was shown in [58] the adsorption energy of counterions decreases when the dilute adsorption layer is simulated. The fact that the co-surfactants do not affect the adsorption constant of counterions is in good agreement with results reported in the literature for ionic-nonionic admixtures adsorption layers where the adsorption energy of counterion is shown that does not depend on the presence of nonionic ad-mixture [61].

The determined dissociation constants are closely related to the salt concentration at which the maximal viscosity in the salt curve is reached, as shown in [21]. That is why, even in presence of different additives,  $C_{MAX}$  is the smallest for  $\text{Ca}^{2+}$  containing solutions and the highest for  $\text{Na}^+$  containing solutions. The linear dependence between  $\ln C_{MAX}$  and  $\ln K_{ads}$  shown in Fig. S12A indicates that  $C_{MAX}$  decreases with the adsorption constant of counterions to the micelle surface for all studied systems (BS, BS+C8OH and BS+C8TAB). It is observed that the

**Table 2**

Dissociation constant,  $K_d$ , adsorption constant,  $K_{ads}$ , thickness of Stern layer,  $\delta$ , minimal area per molecule for LES molecules neutralized with different counterions,  $a_{min}$ ,  $\Delta\mu^0/k_B T$  is dimensionless standard free energy of adsorption of counterions on the micelle surface.

	$K_d$ , mol/kg water	$K_{ads}$ , kg/mol	$\delta$ , nm	$a_{min}$ , nm <sup>2</sup>	$\Delta\mu^0/k_B T$
Na	0.26	3.84	0.72	0.40	3.11
K	0.14	7.14	0.67	0.37	3.88
NH4	0.182	5.45	0.67	0.37	3.61
Mg	0.079*	12.7	0.86	0.32	4.35
Ca	0.050*	20.0	0.82	0.28	4.96

\* Note that  $K_{d(MLES)2}$  is equal to value of  $K_d$  in the table on the power of 2. Here the square root is shown in order to have the same dimension as  $K_d$  for monovalent ions.

presence of co-surfactants only affects the intercept of the linear dependence without changing the slope of the curve. Therefore, the product of  $C_{MAX} K_{ads}^{1.3}$  remains constant of  $2830 \pm 334$  for BS,  $1342 \pm 138$  for BS+ 0.5 wt% C8TAB and  $788 \pm 73$  for BS+ 0.5 wt% C8OH showing that addition of 38.4 mM C8OH decreases 3.6-fold the value of  $C_{MAX} K_{ads}^{1.3}$ , whereas the presence of 19.8 mM C8TAB decreases it 2.1-fold. The addition of 39.6 mM C8TAB decreases  $C_{MAX} K_{ads}^{1.3}$  down to 400 showing that the effect of the presence of cationic co-surfactant has larger impact compared to the effect of C8OH at the same molar concentration.

### 5.2. Width of the distribution and its dependence on counterion energy for adsorption

The other parameter that is very important for salt curves is the width of the distribution. As can be seen from data presented in Table 1 the lower the electrolyte concentration required to induce the micellar growth, the steeper is the viscosity decrease after the maximum. This effect can be easily explained after accounting that the position of maximum depends on the energy for adsorption of counterions to micellar surface. The higher the adsorption energy, the lower the value of  $C_{MAX}$  and the faster decrease in viscosity after the maximum. The scaled width of the distribution,  $C_0/C_{MAX}$  is shown as a function of adsorption energy of counterions in Fig. S12. One sees that the relative width of the distribution decreases with the increase of energy of counterion adsorption for all studied systems. However, the results for BS and BS+C8TAB are very close to each other and the slope of the curve is similar, whereas the dependence is much weaker for C8OH containing solutions. Note that for monovalent ions the salt curves for C8OH containing solution is much narrower compared to BS and BS+C8TAB. This comparison shows unambiguously that the main effect of C8TAB is to neutralize part of SLES molecules, but the interactions between the remaining charged fraction of SLES molecules is not affected by the presence of C8TAB in the micelles, whereas the presence of C8OH affects significantly these interactions.

This unexpected result is most probably related to the ability of alcohol to form complex with LES' via H-bonding [64]. Also, it was shown in Ref. [66] that the mixing of fatty alcohols with chain length of C10 and C12 and SLES and CAPB is energetically favorable, which was explained with the fact that these alcohols can easily adjust their position in the micelle to form a compact palisade layer [66]. Therefore, after the branching these molecules can change their position and facilitates the stress release by forming many branches at the positions they are incorporated. That is why the viscosity decreases very steeply after the maximum and for description of the results we have to account for formation of such complexes and weak points where the branching can occur, see Fig. 5.

### 5.3. Maximal viscosity and its relation to branching of surfactant micelles

SLES+CAPB mixed surfactant system possess higher viscosity compared to a single component solution which is attributed to the difficult branching [24]. The maximal viscosity decreases with the increase the hydration radius of counterion which differs from the results reported for SLES alone [21]. This difference was attributed to the different affinity of sulfate group from SLES and carboxylic group from CAPB to the ions with different hydrated radius. Sulfate group binds strongly to  $\text{NH}_4^+$  than to  $\text{Na}^+$  where the opposite is determined for carboxylic group. As a consequence, the ratio between maximal viscosity reached in presence of  $\text{NH}_4^+$  is around 20 % higher. The similar dependence is observed for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . It should be mentioned that the ratio between SLES and CAPB in the mixture is expected to have significant impact on the maximal viscosity that can be reached in presence of  $\text{NH}_4^+$  and  $\text{Na}^+$ . The maximal viscosity is expected to pass through a maximum as a function of SLES-CAPB mixture and the ratio between maximal viscosity achieved in presence of  $\text{NH}_4^+$  and  $\text{Na}^+$  is expected to

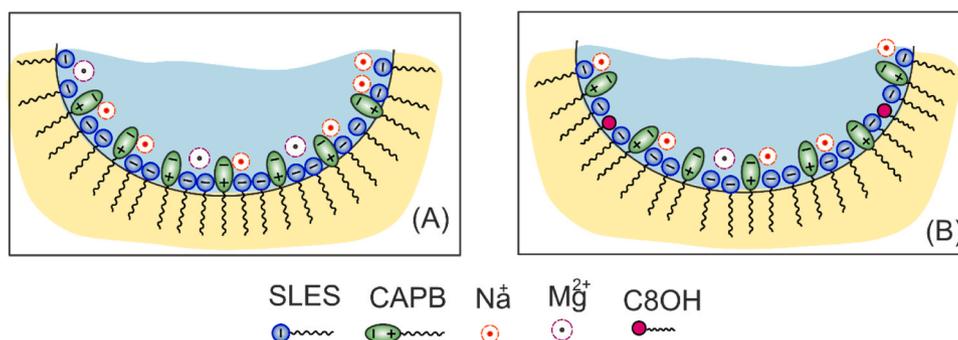


Fig. 5. Schematic representation of the neutralization of SLES molecules at the salt concentration at which the maximal viscosity is reached for (A) BS+Mg<sup>2+</sup> and (B) BS+0.5 wt% C8OH+Mg<sup>2+</sup>. The fraction of ionized molecules is higher for BS+C8OH+Mg<sup>2+</sup> which decreases the probability for branching and increases the maximal viscosity which is reached.

increase with the decrease of fraction of SLES in the mixture. In other words, at lower molar fraction of CAPB in SLES-CAPB mixture the maximal viscosity in presence of Na<sup>+</sup> will be higher than in presence of NH<sub>4</sub><sup>+</sup>, whereas at higher molar fraction of CAPB the viscosity in presence of NH<sub>4</sub><sup>+</sup> will be higher than in presence of Na<sup>+</sup>.

In the current study we showed that the presence of two very different additives, cationic C8TAB and nonionic C8OH, are able to change significantly the electrolyte concentration required to reach the maximal viscosity in SLES-CAPB mixture with fixed ratio. However, in all cases the maximal viscosity in presence of NH<sub>4</sub><sup>+</sup> is the highest, followed by Na<sup>+</sup> and Ca<sup>2+</sup> and the lowest in the presence of Mg<sup>2+</sup> showing that even in presence of co-surfactants the ratio between sulfate groups and carboxylic groups on the micelle surface control the branching. On the other hand, the presence of co-surfactants in SLES+CAPB solution increases the total surfactant concentration in the mixture and increases the value of maximal viscosity that is reached. Eq. (1) which accounts for both the effect of counterions and the total surfactant concentration predicts very well the experimental data obtained with both co-surfactants in presence of monovalent ions with  $q$  value of 2.0 which shows that the branching occurs in a similar way for those systems. However, the value of power law index decreases down to 1.7 for systems with co-surfactants in presence of divalent ions showing more difficult branching in presence of co-surfactants compared to the case when there are no co-surfactants in the solution. The meaning is that the presence of co-surfactant decreases the ability of divalent ions to induce branching in the micelles, which is related to longer distance at which these ions stay in presence of co-surfactant and as such increases the dipole and decreases the probability of branching, see schematic representation in Fig. 5. It should be mentioned also that at the moment at which the branching starts, the fraction of LES molecules that are neutralized by divalent ions is much smaller in the case of systems containing co-surfactants. It decreases from 27 % for BS to 15 % for BS+0.5 wt% C8TAB and down to 9 % for BS+0.5 wt% C8OH when divalent ions are used as counterions. Therefore, the branching is more difficult in presence of co-surfactants because the fraction of divalent ions on the micelle surface is much lower than in the case of BS solution. Note that the effect is even more pronounced for BS+1 wt% C8TAB where the value of  $q$  decreases further to 1.5 showing even more difficult branching because in the stage when packing parameter becomes equal to 0.523 only 5 % of LES molecules are neutralized by divalent ions. Therefore, the branching occurs similarly to the case when monovalent ions are used as counterions because at that stage they prevails on the micelle surface, see Fig. 5.

The presence of Na<sup>+</sup> the effect of C8TAB and C8OH on the fraction of LES<sup>-</sup> molecules is also noticeable, but the fraction decreases from 55 % to 44 % and 36 %, respectively. The relative decrease is much smaller and as consequence the effect of co-surfactants on the branching in presence of monovalent counterions is almost negligible.

The proposed explanation suggests that the effect of co-surfactants

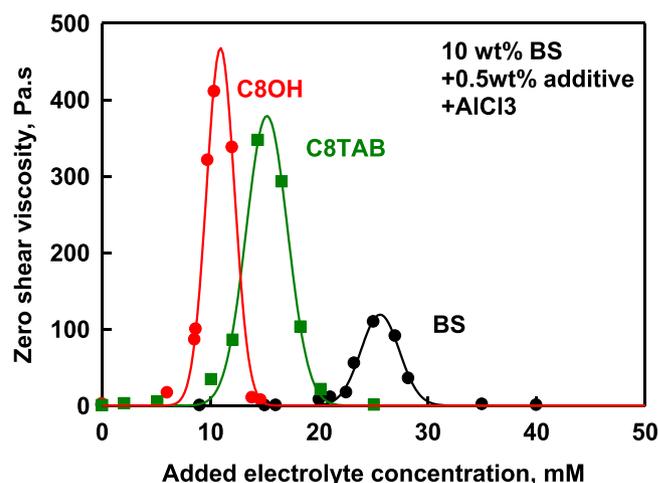


Fig. 6. Zero shear viscosity as a function of added AlCl<sub>3</sub> for 10 wt% BS (black circles), 10 wt% BS + 0.5 wt% C8TAB (green squares) and 10 wt% BS + 0.5 wt% C8OH (red symbols).

will be even more significant for trivalent ions. To test this hypothesis, we performed also experiments with AlCl<sub>3</sub> and found that the maximal viscosity increases from 120 Pa.s (no additive) to 370 Pa.s (in presence of 0.5 wt% C8TAB) and to 470 Pa.s (in presence of C8OH), see Fig. 6. This is showing that for trivalent ions (where the degree of neutralization will be even much more affected) the maximal viscosity becomes closer to one determined in presence of monovalent ions which neutralize the main part of the molecules in presence of co-surfactants.

To account for this interplay between the co-surfactants and counterions we modify Eq. (1) to acknowledge for the different counterions neutralizing the micellar surface to become:

$$R_{\text{avg}} = \frac{(1 - \alpha_1(p = p_{\text{max}}) - \alpha_2(p = p_{\text{max}}))R_{\text{Na}} + \alpha_2(p = p_{\text{max}})R_{\text{M}}}{1 - \alpha_1(p = p_{\text{max}})} \quad (17)$$

Where  $\alpha_1$  and  $\alpha_2$  are the values of the fraction of ionized LES molecules and neutralized by different from sodium counterions at the moment at which the packing parameter reaches the value of  $p_{\text{max}}$ , where the maximum viscosity is reached. In that case the values of  $A$  and  $B$  in Eq. (1) has the values of 17,900 and 39,000 respectively and the value of  $q$  remains equal to 2 for all different systems. In such way we were able to predict the maximal viscosity for all studied systems without changing the value of  $q$  in Eq. (1).

## 6. Conclusions

A systematic series of experiments was performed to determine the

effects of two co-surfactants: trimethyl-1-octylammonium bromide (C8TAB) and 1-octanol (C8OH) on the rheological properties of a mixture of anionic sodium laureth sulfate (SLES) and zwitterionic cocoamidopropyl betaine (CAPB) at 2:1 ratio. The study was carried out in the presence of four different salts: two monovalent (sodium and ammonium) and two divalent (calcium and magnesium) chlorides. The theoretical model developed by Pleines et al. [21] was extended to account for the competitive adsorption between monovalent and divalent counterions and was used to describe the experimental data. This model extension accurately predicts the salt curves for different salts and co-surfactant concentrations, allowing for a better understanding of the mechanisms driving the experimentally observed effects.

The results showed that the salt concentration required to achieve maximal viscosity in the salt curve is the lowest with  $\text{Ca}^{2+}$  and the highest with  $\text{Na}^+$  as counterions. The theoretical model shows that this variation is due to the much higher adsorption constant of  $\text{Ca}^{2+}$  compared to  $\text{Na}^+$  on the micelle surface. A good agreement was found between the adsorption energies determined in the literature via molecular dynamics simulations [58] and those obtained in the current study, indicating that counterion adsorption on the micellar surface is similar to their adsorption in the adsorption layers formed on air-water interface.

The theoretical model shows that the presence of the studied additives does not alter the adsorption energy of counterions on the micellar surface but significantly reduces the salt concentration needed to induce micellar growth. This effect is attributed to the ability of cationic C8TAB to neutralize anionic SLES without altering the area per molecule for neutralized and ionized molecules on the micellar surface. The incorporation of C8OH between SLES and CAPB molecules decreases the average area per molecule and reduces the fraction of SLES molecules that need to be neutralized to achieve the packing parameter at which maximal viscosity is reached.

The reduction in the required salt concentration to achieve maximal viscosity in the presence of C8TAB and C8OH is accompanied by a significant increase up to 4-times in the maximal viscosity observed in the salt curves. This result is unexpected, as most studies report an inverse relationship [21–24]: lower salt concentrations typically correlate with lower maximal viscosity. The increased viscosity in the presence of co-surfactants is more pronounced for divalent and trivalent counterions. The theoretical model shows that an increased fraction of divalent ions decreases the maximal viscosity that can be reached by facilitating branching. In contrast, when co-surfactants are present on the micelle surface, the optimal packing parameter is achieved at a much smaller fraction of adsorbed divalent counterions, resulting in a much higher maximal viscosity.

The proposed model opens new avenues for a deeper understanding of the phase behavior of surfactant mixtures widely used in practical applications, such as shampoo and detergent formulations. Furthermore, the conclusions drawn from this work could facilitate future research aimed at predicting the phase behavior of various anionic-zwitterionic surfactant mixtures and accelerating the development of formulations with more eco-friendly surfactants.

Future work could involve extending this approach further by performing molecular dynamics simulations to determine the adsorption energies of various counterions and incorporating these findings into the proposed model to predict salt curves for diverse surfactant and salt mixtures.

#### CRedit authorship contribution statement

**Zlatina Mitrinova:** Data curation, Investigation, Writing – original draft. **Zhuljeta Valkova:** Investigation, Writing – review & editing. **Slavka Tcholakova:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Supervision, Validation, Visualization, Writing – review & editing.

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#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2024.135943](https://doi.org/10.1016/j.colsurfa.2024.135943).

#### Data availability

Data will be made available on request.

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