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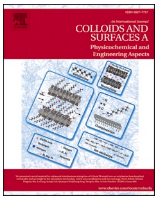

Cosurfactants for controlling the surface properties of diluted solutions: Interplay with bulk rheology of concentrated solutions

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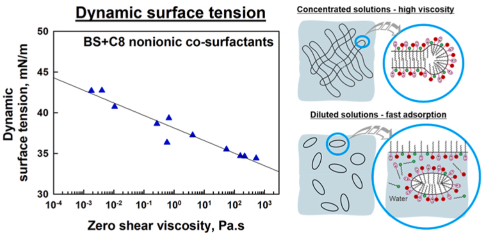
GRAPHICAL ABSTRACT



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ABSTRACT

The effect of the fatty alcohols (C_nOH), fatty acids (C_nAc), alkyltrimethyl ammonium bromides (C_nTAB), alkyl sulfates (C_nSO_4Na) and alkyl acetates (C_nAcet), with n varied between 6 and 12 C-atoms, on the surface properties of 0.5 wt% mixed solutions of sodium laurylether sulfate (SLES) and cocoamidopropyl betaine (CAPB) was studied. It was shown that the equilibrium surface tension decreases with increasing the cosurfactant chain-length. For example, the addition of $C_{12}OH$ to SLES+CAPB solution decreases its surface tension from 29 down to 22 mN/m. Both the dynamic surface tension and the characteristic adsorption time pass through a deep minimum when cationic or nonionic cosurfactants with 8 or 10 C-atoms are added. The minimum is particularly deep for nonionic surfactants with small head group (acids and alcohols) which destabilize the micelles and increase the rate of surfactant adsorption. The addition of anionic cosurfactants does not change the dynamic and equilibrium surface tensions of SLES+CAPB system. A strong correlation between the dynamic surface tension of diluted surfactant solutions (0.5 wt%) and the viscosity of the respective concentrated solutions (10 wt%) is established and explained for nonionic cosurfactants.

1. Introduction

The anionic surfactant sodium laurylether sulfate (SLES) and the zwitterionic cocoamidopropyl betaine (CAPB) are widely used in various formulations for personal care, such as shampoos, body washes, creams and lotions [1–5]. Therefore, their surface and foam properties are widely studied in the literature [6–11]. In our previous study [1] we investigated the effect of a wide range of cosurfactants on the rheological properties of concentrated solutions (10 wt%) of surfactant mixrures SLES+CAPB+cosurfactant. We showed that the medium-chain cosurfactants with compact head-group have the largest effect on the rheological properties of the concentrated solutions [1]. When

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cosurfactants with same head-group are compared, the highest viscosity is measured with solutions containing cosurfactants with chain-length of 8–10 carbon atoms. The increasing number of double bonds and/or branching of the cosurfactant tails reduces the effect of the cosurfactant addition on the solution viscosity.

In the current paper we study the same series of cosurfactants as in Ref. [1]. However, the focus is currently on the effect of these cosurfactants on the dynamic and equilibrium surface tensions of diluted solutions (0.5 wt%) which are encountered in the practical applications of the surfactant solutions, such as foaming [12–26], antifoaming [27], impact of the drop with solid surface [28–30], size of the drops in spraying [31], etc.

Patist et al. showed that cosurfactants, such as fatty alcohols (C_nOH) and alkyltrimethylammonium bromides (C_nTAB), affect the stability of sodium dodecylsulfate (SDS) micelles, as well as the foamability and the foam stability of the mixed surfactant solutions [18,32]. The stability of the micelles passes through a maximum, as a function of the chain-length for both C_nOH and C_nTAB at 12 C-atoms, which are equal to the number of C-atoms of the main surfactant (SDS). The higher micellar stability corresponds to maximum in the dynamic surface tension of SDS+$C_{12}OH$ [18], whereas the equilibrium surface tension has a minimum for SDS+$C_{12}TAB$ solutions [33] when compared to SDS alone. The tighter packing of the molecules inside the surfactant micelles decelerate the rate of surfactant supply to the surface, while the tighter packing of the molecules in the equilibrium adsorption layers reduces the equilibrium surface tension. It was shown in Ref. [18] that the total surfactant concentration also has significant impact on the effect of cosurfactants – at lower concentration of 15 mM SDS all added C_nOH with n varied between 8 and 16 leads to higher stability of the surfactant micelles, whereas at high surfactant concentration of 150 mM SDS all alcohols except $C_{12}OH$ decrease the micellar stability due to the mismatch of the surfactant and cosurfactant alkyl chains [18]. On the other hand, in our previous study [7] we showed that the addition of fatty acids, C_nAc (with n varied between 8 and 18), leads to a significant increase in the viscosity of concentrated SLES+CAPB solutions (10 wt%) when C_8Ac and $C_{10}Ac$ are added. In the same study [7] we showed that the fatty acids decrease the dynamic surface tension of the respective diluted surfactant solutions (0.5 wt%) and increase their foamability. On the other hand, long-chain fatty acids with $n = 14$ or 16 do not change significantly the viscosity of the concentrated solutions (10 wt%) and the dynamic surface tension of diluted solutions (0.5 wt%), while these fatty acids are very efficient in decreasing the equilibrium surface tension of diluted solutions by forming condensed adsorption layers at the air-water interface.

The major aim of the current study is to clarify and quantify the effect of various cosurfactants with chain-lengths varied between 6 and 12 C-atoms and with different head-groups (anionic, cationic, nonionic) on the dynamic and equilibrium surface tensions of diluted (0.5 wt%) SLES+CAPB solution. In addition, we compare and clarify the relation between the surface properties of the diluted SLES+CAPB solutions (0.5 wt%) with the viscosity of the respective concentrated solutions (10 wt %). To achieve our aims, we study systematically the effect of C_nTAB, C_nOH, C_nAc, C_nAcetates, C_nSulfate and C_nAminooxides with straight saturated chains and n varied between 6 and 12 C-atoms. For comparison, we study also the effect of fatty alcohols with double bonds or/and branching in their tails. The results obtained in the current study are compared with the results about the viscosity of the respective concentrated solutions, described in Ref. [1].

2. Materials and methods

2.1. Materials

The basic surfactant system, denoted as BS in the text, is a mixture of sodium laurylether sulfate, SLES (product of Stepan Co., IL, USA; commercial name STEOL CS-170 Stepan) and cocoamidopropyl betaine, CAPB (product of Goldschmith, commercial name Tego Betaine F50). The concentrated surfactant solutions contain 10 wt% SLES+CAPB, at fixed weight ratio of 2:1, corresponding to approx. 200 mM SLES and 100 mM CAPB [1]. Different cosurfactants were added by dissolving 1 wt% of cosurfactant into 10 wt% stock solution of the main surfactant. The cosurfactants were chosen according to our previous work [1] and some of their properties are described in Table 1. Most of the surfactant solutions were prepared at room temperature and the components were dissolved under mild stirring until clear solution was formed. Some of the additives, incl. fatty acids, fatty alcohols with chain length between 8 and 12 carbon atoms, sodium alkylsulfate, sodium octylsulfonate and octylgallate were dissolved at 40 °C under mild stirring, until a homogeneous solution was obtained (after ca. 1 h). The stock solutions were kept at room temperature for further studies and appeared stable for several months after their preparation.

One should note that the concentrated solutions (SLES+CAPB+cosurfactant) contain also 112 mM NaCl coming from the CAPB synthesis [34]. The diluted solutions were prepared just before the surface tension measurements by mixing 1 part of the concentrated solution with 19 parts of deionized water or with 19 parts of 112 mM NaCl solution. Therefore, the studied solutions contained 0.5 wt% SLES+CAPB, 0.05 wt% cosurfactant and 5.6 mM or 112 mM NaCl.

2.2. Viscosity, equilibrium and dynamic surface tensions of the diluted surfactant solutions

All diluted solutions behaved as Newtonian liquids with low viscosity, η, which was measured with thermostated capillary viscometer, after calibration with pure water. The equilibrium surface tension (EST) of the diluted solutions, σ, was measured by Wilhelmy plate method on tensiometer K100 (Kruss GmbH, Germany) for a period of 900 s. The dynamic surface tension (DST) of the diluted solutions was measured via maximum bubble pressure method (MBPM) on tensiometer BP2 (Kruss GmbH, Germany) adapted with glass capillary [35]. Note that the concentrated solutions (10 wt%) have non-Newtonian behavior; however, after dilution to 0.5 wt% they become Newtonian liquids with viscosity close to that of pure water, see Table 1.

All experiments were performed at $T = 20$ °C.

2.3. Micelles size determination by dynamic light scattering

Micelles diameters in the diluted solutions were measured on goniometric light scattering apparatus Malvern 4700 C (Malvern Instruments UK). Solid-state laser with wavelength of 532 nm was used as a light source and the experiments were performed at 90° scattering angle, with additional measurements at 60° and 120° for verification. The temperature was set to 20 °C in all measurements.

From the measured autocorrelation function of the scattered light, the instrument calculates the distribution of the diffusion coefficients, D, of the molecular aggregates in the solution. Next, the hydrodynamic diameters of these aggregates are determined using the Stokes–Einstein equation:

$$d_h = kT/3\pi\eta D \qquad (1)$$

where k is Boltzman constant; T is absolute temperature, and η is dynamic viscosity of the medium. The volume averaged values of the aggregate diameters are used to compare the results for the different systems.

3. Experimental results

3.1. Viscosity of the diluted solutions and micelle size

The viscosities of diluted solutions (0.5 wt%) varied between 0.9 and 1.2 mPa.s and were very close to the viscosity of the diluted BS solution,

Table 1
Studied systems and properties of diluted solutions. Molecular mass of SLES is 332 g/mol and molecular mass of CAPB is 342 g/mol.

Abbrev.	**Head group**	**Chain length**	**Molecular mass, g/mol**	**Properties of diluted solutions (0.5 wt%)**			
				pH	**Solution viscosity, mPa.s**	**Micelle diameter, nm**	**Concentration of cosurfactant, mM**
–	–	–		5.9	0.99	3.3 ± 0.4	0
C_nTAB	$N^+(CH_3)_3(Br)^-$	6	224.2	5.9	N.M.	3.1 ± 0.2	2.2
		8	252.2	6.0	1.00	2.6 ± 0.4	2.0
		10	280.3	6.0	1.04	4.8 ± 0.8	1.8
		12	308.3	6.0	N.M.	4.7 ± 0.3	1.6
C_nOH	OH	6	102.2	5.8	1.03	2.0 ± 0.2	4.9
		7	116.2	6.0	N.M.	N.M.	4.3
		8	130.2	6.0	1.02	2.6 ± 0.1	3.8
		8_1	128.2	6.2	N.M.	N.M.	3.9
		9	144.3	5.9	N.M.	N.M.	3.5
		10	158.3	6.0	1.03	4.5 ± 0.6	3.2
		12	186.3	6.0	N.M.	N.M.	2.7
Citronellol	OH	8	156.3	5.9	1.18	1.7 ± 0.1	3.2
Linalool	$C(CH_3)$ (OH) $CHCH_2$		154.3	5.9	1.16	3.9 ± 0.8	3.2
Citral	CH_2O		152.2	6.0	1.05	1.4 ± 0.6	3.3
C_nAc	COOH	6	116.2	4.5	N.M.	N.M.	4.3
		8	144.2	4.7	0.91	2.5 ± 0.3	3.5
		10	172.3	5.3	0.91	4.4 ± 0.9	2.9
		12	200.3	5.8	N.M.	N.M.	2.5
C_8G	$OOCC_6H_2(OH)_3$	8	282.3	6.1	1.03	3.3 ± 0.2	1.8
C_nAcet	$OCOCH_3$	6	144.2	5.8	1.02	3.3 ± 1.1	3.5
		8	172.3	5.8	0.85	3.2 ± 0.4	2.9
		10	200.3	5.9	0.88	3.0 ± 0.2	2.5
C_8M	$COOCH_3$	8	158.2	5.7	0.89	3.9 ± 0.5	3.2
$PEGC_8$	$[OCH_2CH_2]_nOH$	8		5.9	1.00	4.0 ± 0.8	Not known[a]
$C_{10}AO$	$N^+\text{->}O^-(CH_3)_2$	10	201.4	8.1	0.99	2.8 ± 0.1	2.5
C_8NaSO_3	$OSO_2^-Na^+$	8	216.3	6.0	0.91	3.5 ± 0.1	2.3
C_nNaSO_4	$OSO_3^-Na^+$	8	232.3	6.2	1.01	4.4 ± 0.8	2.2
		10	260.3	5.9	0.88	3.0 ± 0.4	1.9

N.M. - not measured.

[a] - the molecular mass of $PEGC_8$ is not provided and we cannot calculate the molar concentration of this cosurfactant in the diluted solution.

see Table 1. Despite the presence of entangled worm like micelles (WLM) in the respective concentrated solutions (10 wt%) which increase the viscosity up to 500 Pa.s, the micelles became spheroidal upon dilution. The micelle concentration in the diluted solutions is below the overlapping one, the micelle size is below 5 nm and, therefore, the solution viscosity is close to that of pure water, see Table 1.

3.2. Dynamic and equilibrium surface tensions

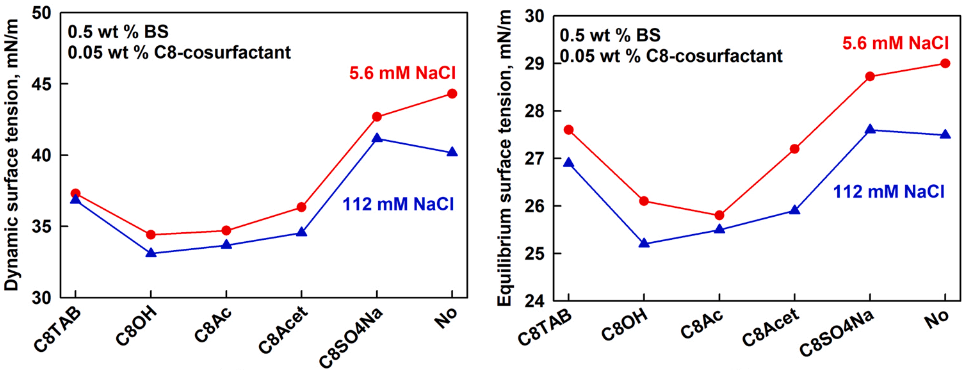
The surface tension as a function of time is shown in Fig. S1A and B, as measured by the MBPM and Wilhelmy plate methods, respectively, for diluted solutions of BS and some BS+cosurfactant combinations. The surface tension measured by MBPM decreases significantly with time, whereas the surface tension measured by the Wilhelmy plate method remains almost constant during the entire period of measurement. To compare the effects of the various cosurfactants on the dynamic surface tension we determined the surface tension measured after 100 ms by the MBPM, which is close to the characteristic time for bubble formation in Barstch foaming test, as shown in our previous studies [12,13]. In Section 4 below the experimental curves from the MBPM are processed computationally to extract further information about the adsorption kinetics. To compare the equilibrium surface tensions of the various solutions, we used the surface tension measured after 900 s by Wilhelmy plate method. The experimental data for the dynamic and equilibrium surface tensions of the solutions containing different cosurfactants are shown in Fig. S2 in Supporting information.

3.3. Effect of electrolyte

It is well known from the literature that the addition of electrolyte affects strongly the surface properties of the ionic surfactants by screening the electrostatic repulsion between the charged surfactant molecules [35,36]. As explained above, the concentrated surfactant solutions contain 112 mM NaCl coming from the CAPB synthesis [34], which decreases down to 5.6 mM upon dilution with pure water. To clarify the effect of this neutral electrolyte on the micelle properties we compared the properties of diluted surfactant solutions which were prepared with pure water and with 112 mM NaCl solution. These experiments were performed with solutions containing cosurfactants with 8 C-atoms in their tails (and several different head-groups), because these cosurfactants have the largest effect on the viscosity of the concentrated 10 wt% solutions [1]. The obtained results are shown in Fig. 1. One sees that the increase of NaCl concentration from 5.6 mM to 112 mM NaCl leads to decrease of the dynamic and equilibrium surface tensions for all studied systems, due to the screened electrostatic interactions between the adsorbed molecules. The effect of NaCl is the smallest for the solutions containing C_8TAB which shows that the presence of cationic cosurfactant already decreases the electrostatic repulsion between the SLES molecules. The effect of NaCl is the largest for BS without cosurfactants, because the SLES molecules repel each other significantly at low NaCl while forming denser adsorption layers at higher NaCl concentration.

3.4. Effect of pH

For most of the diluted solutions, pH varied between 5.8 and 6, see Table 1, which is attributed to the main SLES+CAPB components [7]. However, when fatty acids C_6Ac, C_8Ac and $C_{10}Ac$ are added as cosurfactants, the solution pH decreases down to 4.5. When $C_{10}AO$ is added as cosurfactant, the pH increases to 9.3. To clarify the effect of pH on the properties of FAc-containing solutions, the pH was adjusted to 6.0 by addition of NaOH. For BS+$C_{10}AO$ solution the pH was adjusted to 7.0 by adding HCl. The experimental results for solutions with natural and adjusted pH values are compared in Table 2. Interestingly, both DST and



(A) (B)

Fig. 1. (A) Dynamic surface tension after 100 ms and (B) Equilibrium surface tension as a function of cosurfactant type at dilution with: 5.6 mM NaCl (red circle) and 112 mM NaCl (blue triangles). All cosurfactants have 8 carbon atoms in their hydrophobic tails.

Table 2
Dynamic and equilibrium surface tensions of diluted solutions, containing 0.5 wt% SLES+CAPB and 0.05 wt% cosurfactant at different pH values. The viscosity of the respective concentrated solutions is also shown.

Solution	Concentrated solutions (10 wt %)		Diluted solutions (0.5 wt%)		
	pH	Viscosity, Pa.s	pH	DST after 100 ms, mN/m	Equilibrium surface tension, mN/m
BS		0.007	5.9	44.3	29.0
BS+C8Ac	5.2	101.5	4.7	33.6	25.8
	6.0	149.0	6.0	40.2	28.4
BS+C10Ac	5.5	9.8	5.3	33.1	24.1
	6.0	96.1	6.0	35.7	25.8
BS+C8Amine			9.4	33.4	25.9
			7.3	35.1	25.8
BS+C10Amine			9.3	40.5	24.6
			7.1	40.4	24.7

EST for FAc-containing solutions increase with the increase of pH. Similar results were obtained with long-chain fatty acids C_{12}Ac-C_{16}Ac in our previous study [6] for the equilibrium adsorption layers. The latter results were explained with stronger electrostatic repulsion between the charged FAc and SLES molecules at higher pH, which leads to more diluted equilibrium adsorption layers and to higher equilibrium surface tension. The higher DST at high pH for BS+FAc could be explained by two possible phenomena: (1) Under the assumption that the FAc molecules are present in the dynamic adsorption layers, the increase of pH leads to their ionization and to electrostatic repulsion with the main surfactant, SLES, thus reducing the rate of adsorption and the amount of adsorbed FAc; (2) The ionized FAc molecules at higher pH are less prompt to incorporate inside the surfactant micelles; as a consequence, the mixed SLES+CAPB+FAc micelles contain less FAc at higher pH and have properties close to those of SLES+CAPB micelles. In other words, when nonionized cosurfactant molecules are present in the solution, they are incorporated inside the micelles and due to the mismatch in the chain-length with the main surfactants (SLES and CAPB) the mixed micelles are disturbed and faster de-micellization process is observed [7]. In contrast, the fatty acids act as anionic additives at high pH and no significant effect on the DST is observed.

To check for possible effect of pH on the properties of the wormlike micelles in the concentrated 10 wt% solutions, the viscosity of the concentrated solutions at two different pH values was measured, see Table 2. One sees that the viscosity of the concentrated solutions is lower at lower pH, which shows that the main effect of pH on the DST is related to the electrostatic repulsion between the adsorbed molecules, viz. to effect (1) as described in the previous paragraph. Effect (2) would lead to an opposite trend in concentrated solutions – viz. to higher viscosity at lower pH when the FAc molecules are less ionized.

One the other hand, pH does not change significantly the DST or the equilibrium surface tension of BS+C_{10}AO and BS+C_8AO solutions. These results mean that these cosurfactants behave as nonionic in the studied pH range, in agreement with the known pKa $\approx$ 4.1 for C_{12}AO.

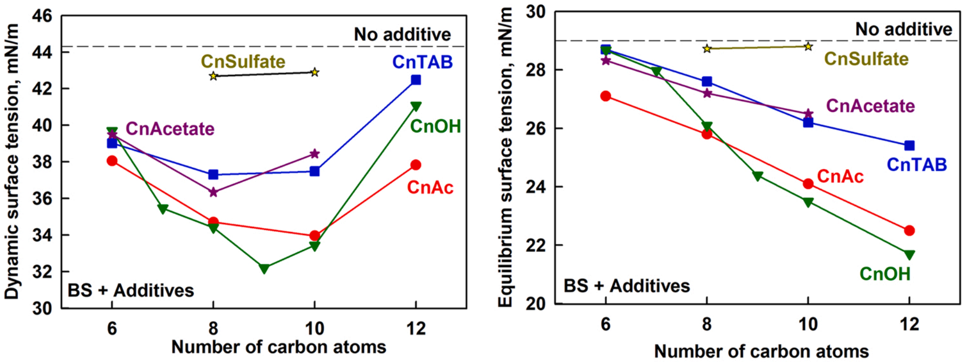
From these experiments we can conclude that the increase of pH for FAc-containing solutions decrease their effect on the dynamic and equilibrium surface tension of BS solution, due to the FAc ionization and the related decrease in the FAc adsorption, due to the electrostatic repulsion with the adsorbed SLES molecules.

3.5. *Effect of cosurfactant chain length*

The effect of cosurfactant chain length on the dynamic and equilibrium surface tensions of BS solution is illustrated in Fig. 2. One sees that the addition of anionic cosurfactants C_nSulfates with $n = 8$ or 10 does not change either the equilibrium or dynamic surface tensions of BS solution. The anionic cosurfactants of this type do not induce formation of WLM and the viscosities of the concentrated solutions containing C_8Sulfate and C_{10}Sulfate are lower when compared to the viscosity of BS solution. The dynamic and equilibrium properties of the adsorption layers formed from diluted solutions are also controlled by the main surfactants SLES and CAPB only.

The dynamic surface tension passes through a minimum when plotted as a function of the surfactant chain-length for C_nAc, C_nTAB, C_nOH and C_nAcetates, whereas the equilibrium surface tension decreases monotonously with increasing the chain-length of all these classes of cosurfactant. These different trends indicate a significant difference in the compositions of the dynamic and equilibrium adsorption layers, respectively. The steady decrease of the equilibrium surface tension for nonionic and cationic cosurfactants with the increase of their chain-length is related to the formation of mixed adsorption layers. When the main surfactants and the cosurfactants are with similar chain-length, they form adsorption layers with closely packed molecules and low equilibrium surface tension. The lower equilibrium tension is reached when nonionic cosurfactants with small head-groups are added.

Minimum in the DST is observed at cosurfactant chain-length of C_8 and C_{10} for most types of cosurfactants, except for the anionic ones, see Fig. 2A. This minimum in the dynamic surface tension corresponds very well to the maximum in the viscosity of the respective concentrated solutions (10 wt%) reported in our previous study [1]. The incorporation of C_8 cosurfactants in the cylindrical part of the wormlike micelles in the concentrated solutions leads to increased micelle length and higher viscosity. Upon dilution of these concentrated solutions, the mismatch in the chain-lengths of the cosurfactant and the main surfactant molecules disturbs the spheroidal micelles which exhibit shorter demicellization time. As a result of this molecular mismatch, the



(A) (B)

Fig. 2. (A) Dynamic surface tension and (B) Equilibrium surface tension as functions of the cosurfactant chain-length for various cosurfactants studied: C_nSulfate (yellow stars), C_nTAB (blue squares), C_nAcetate (purple stars), C_nAc (red circles), C_nOH (green triangles). Dashed line represents the referent SLES+CAPB system without cosurfactant. These solutions contain 0.5 wt% SLES+CAPB and 0.05 wt% cosurfactant.

surfactant molecules adsorb faster on the solution surface and decrease the DST. The same optimal mismatch in the surfactant/cosurfactant chain-lengths is observed for both the viscosity increase of concentrated solutions and for DST decrease of diluted solutions.

3.6. Effect of branching

We studied the effect of surfactant tail architecture at fixed number of carbon atoms in the main chain (C8) for SLES+CAPB+cosurfactant systems. One sees that the presence of double bonds and branching in the cosurfactant chain leads to increase in both the dynamic and equilibrium surface tensions, Fig. 3. This trend could be explained with the steric hindrance created by these non-straight molecules which leads to looser packing in the micelles and in the adsorption layers. At certain degree of branching and large number of double bonds (cf. Citral and Linalool) the equilibrium surface tension becomes equal to that of SLES+CAPB (without cosurfactant) which shows that such branched and/or double bond-containing molecules are not incorporated in the equilibrium adsorption layer. For the same systems, however, the dynamic surface tension remains much lower as compared to that of SLES+CAPB. The latter effect is related to the incorporation of these cosurfactant molecules in the surfactant micelles, thus disturbing the micelles and inducing faster supply of SLES and CAPB from the micelles.

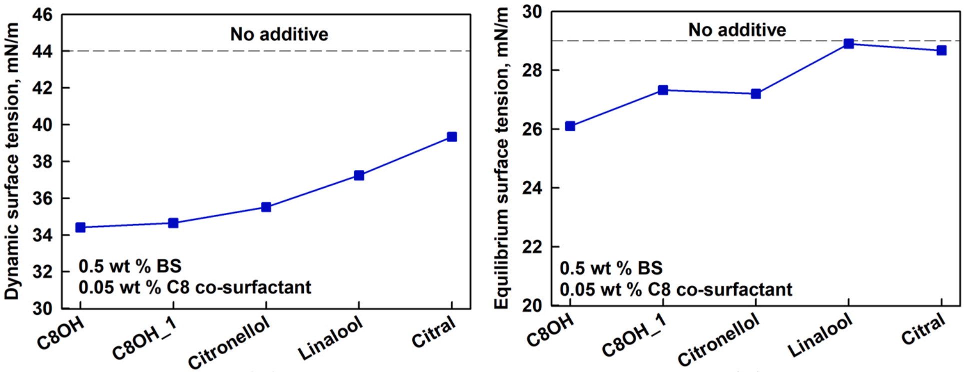
The incorporation of Linalool and Citral in the micelles is proven by their ability to increase the viscosity of the concentrated 10 wt% solutions and to decrease the dynamic surface tension of the diluted 0.5 wt% solutions. However, at equilibrium these molecules stay incorporated inside the micelles. Because their concentration is relatively low, the chemical potentials of the main surfactants are not affected strongly by the presence of the cosurfactant molecules and the latter do not affect the equilibrium surface tension.

3.7. Effect of head-group type

The effect of head-group type is illustrated in Fig. 4. One sees interplay between the cosurfactant head group and the cosurfactant chain-length. All studied C_6 cosurfactants decrease the dynamic surface tension in a similar manner – from 44 mN/m down to ca. 39 mN/m and have no effect on the equilibrium surface tension, except for C_6Ac which decreases the latter from 29 mN/m down to 27 mN/m. On the other hand, the effect of the C_8 and C_{10} cosurfactants on the DST and equilibrium surface tension depends very significantly on the head-group of the cosurfactant. Strongest effect is observed with cosurfactants having small head-group (-OH and -COOH) which decrease significantly both the dynamic and equilibrium surface tensions. The cationic cosurfactants and the nonionic cosurfactants with bulky head-groups have similar effect, whereas the anionic cosurfactants have almost no effect on both the dynamic and equilibrium surface tensions.

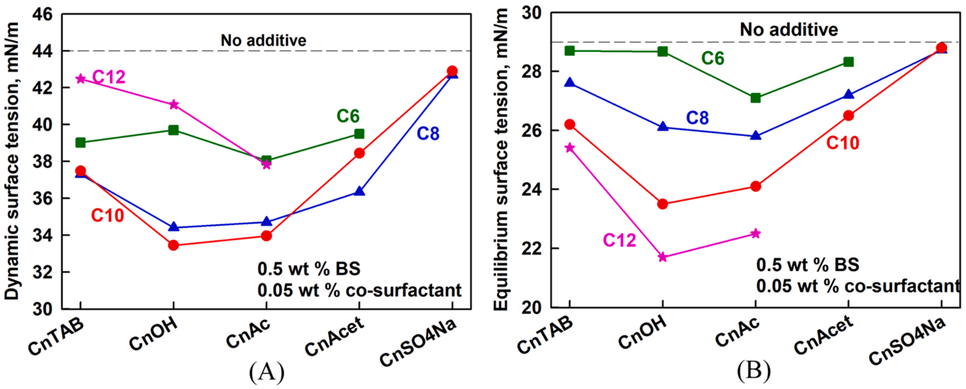
4. Correlations between bulk and surface properties

The lower dynamic surface tension could be explained with the formation of unstable micelles having shorter lifetime [7]. In our previous study we analyzed the effect of several fatty acids on the rheological properties of concentrated 10 wt% SLES+CAPB solutions and found that the cosurfactants inducing the formation of entangled WLM (high viscosity) lead to lower dynamic surface tension of the respective diluted 0.5 wt% solutions [7]. To check whether this trend is robust for



(A) (B)

Fig. 3. (A) Dynamic surface tension and (B) Equilibrium surface tension as functions of the presence of double bonds. Systems contain 0.5 wt% SLES+CAPB and 0.05 wt% cosurfactant.



(A) (B)

Fig. 4. (A) Dynamic surface tension and (B) Equilibrium surface tension for various cosurfactant head-groups. These results are obtained with solutions containing 0.5 wt% SLES+CAPB and 0.05 wt% cosurfactant. Symbols denote: C_{12} (pink stars), C_6 (green squares), C_8 (blue triangles), C_{10} (red circles). Dashed line represents the referent SLES+CAPB system.

other cosurfactants, we correlated the surface properties of the diluted solutions with the bulk rheological properties of the respective concentrated solutions, see Fig. 5. Note that the diluted solutions have Newtonian behavior and viscosity close to that of water, whereas some of the concentrated solutions are very viscous and even can form gels. One sees from Fig. 5A that samples with higher zero-shear viscosity possess lower dynamic surface tension. Note that the results for C_nTAB and octylgallate are excluded from this graph due to their significant deviation from the general correlation.

In Fig. 5B we show the correlation plot for the largest set of additives with the same chain length (C_8), including C_8TAB and C_8gallate. It appears that the data for the latter are separated from those of all other systems and lay around the same line with the referent SLES+CAPB system which is shifted upwards when compared to the other systems. For cationic surfactants there is a strong electrostatic interaction with the anionic SLES molecules, while C_8gallate forms hydrogen bonds between its OH groups and the SLES and CAPB molecules. Most probably, these specific interactions affect the properties of the mixed micelles, containing cationic and gallate-based cosurfactants.

One can conclude from these correlation plots that the formation of mismatched micelles (with respect to the surfactant/cosurfactant chain-length) after dilution of the viscous concentrated solution leads to faster release of monomers from these micelles and to lower dynamic surface tension. This correlation breaks to some extend when strong attraction between the main surfactant and the cosurfactant is realized, as in the C_nTAB-containing diluted solutions.

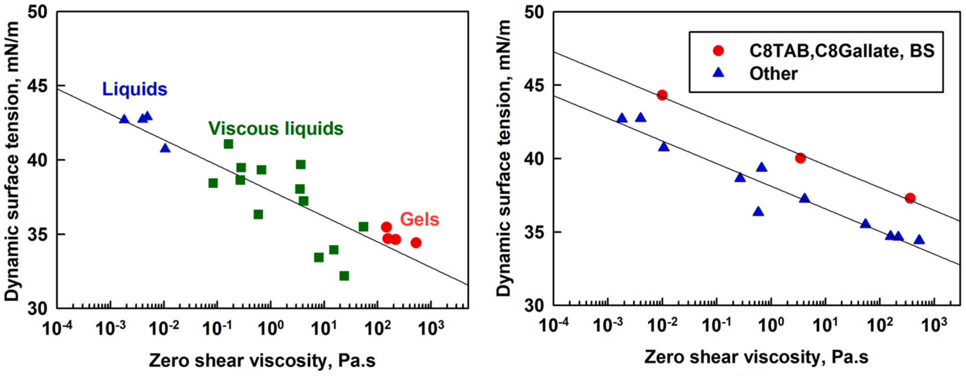
The existing correlations indicate that the measured properties of the concentrated and diluted solutions are affected by a similar phenomenon – the mismatch of the molecular chain-lengths and the related packing in the mixed micelles, affected also by the structure and charge of the head-groups involved. The most effective co-surfactants are the nonionic ones with small head-groups (fatty acids and alcohols) for which WLM are formed and the viscosity increases sharply at high surfactant concentration [1]. For diluted surfactant solutions, in which the micelle concentration is well below the overlapping one, the micelles are spheroidal but loosely packed, which ensures their shorter lifetime and faster surfactant adsorption.

To determine the characteristic adsorption time for the various solutions, we fitted the experimental data obtained from MBPM using the equation derived in Ref. [35] under the assumption for diffusion-limited adsorption:

$$\sigma = \sigma_{EQ} + \frac{S_\sigma}{a_\sigma}\frac{1}{1+\sqrt{t_u/a_\sigma{}^2}} \qquad (2)$$

where t_u is the universal time, representing the experimental time divided by coefficient which accounts for the specific apparatus, s_σ/a_σ accounts for the difference between the initial and the equilibrium surface tensions (viz. for the surface tension decrease), and a_σ^2 is the characteristic time for surface tension lowering. Hence by fitting σ vs. t_u with Eq. (2), a_σ and s_σ are determined as adjustable parameters, whereas σ_{EQ} was determined by the independent Wilhelmy plate measurement. For all studied systems, the fits to the experimental kinetic curves with Eq. (2) are with correlation coefficients $r^2 \geq 0.99$.

The determined values of the characteristic times, as a function of the chain-length of the cosurfactants, are compared in Fig. 6. The shortest



(A) (B)

Fig. 5. Dynamic surface tension measured after 100 ms as a function of zero shear viscosity for (A) all studied systems without C_nTAB and C_8Gallate and (B) BS+C_8additives for C_8TAB, C_8Gallate, BS only (red circles) and other studied systems (blue triangles). Systems contain 0.5 wt% SLES + CAPB + 0.05 wt% additive. Rheological data are taken from ref. 1.

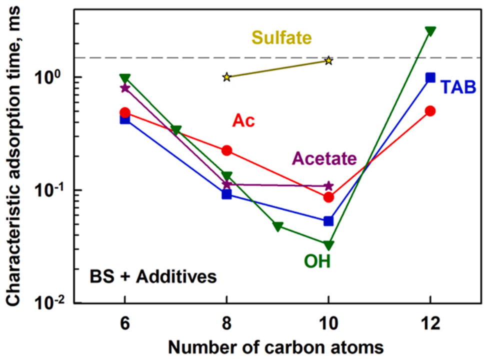


Fig. 6. Characteristic adsorption time as a function of chain length. Systems contain 0.5 wt% SLES + CAPB + 0.05 wt% additive. Symbols are denoted as follows: Sulfate (yellow stars), CnTAB (blue squares), CnAcetate (purple stars), CnAc (red circles), CnOH (green triangles). Dashed line represents referent system SLES+CAPB.

characteristic adsorption time is determined for C_{10} additives with small head-group (fatty acid and fatty alcohol). As discussed above, for these systems the cosurfactants incorporate easily in the surfactant micelles, but the chain-length mismatch ensures shorter lifetime of the micelles. The presence of anionic cosurfactants does not affect the adsorption parameters.

One should note that there are some noticeable differences between the systems diluted with water and with NaCl solution. The latter leads to lower dynamic surface tension at 100 ms and to longer adsorption times, see Fig. S3. The difference is the biggest for C_{10} additives (C_{10}TAB, C_{10}OH, C_{10}Ac). The electrolyte affects significantly the molecular interactions and the higher ionic strength at 112 mM NaCl screens the head-group repulsion, thus leading to tighter molecular packing in the micelles and slower release of monomers from them.

The other parameter that could be correlated with the DST is LogP which is associated with the molecules' hydrophobicity [37]. In Fig. S4 we show the characteristic times, as a function of LogP. As explained in Ref. [1] there is no single master curve for the viscosity of the concentrated solutions vs. LogP and the data pass through a maximum at intermediate logP for all classes of cosurfactants. The situation is similar for the characteristic adsorption time (passing through a minimum) and there are two different curves – one describing the cationic cosurfactants and another one for the nonionic ones. These trends prove that for all studied classes of cosurfactants, there is an optimum cosurfactant hydrophobicity for inducing micellar growth in concentrated solutions and for fast adsorption kinetics in diluted solutions.

On the other hand, the properties of the equilibrium adsorption layers are controlled mainly by the ability of the cosurfactants to pack well in the adsorption layers. As a consequence, the cosurfactants with longer straight chains are able to decrease to larger extend the equilibrium surface tension of the mixed solutions.

5. Conclusions

The effect of cosurfactants having different chain lengths (between 6 and 12) and different head groups (anionic, nonionic and cationic) on the surface properties of SLES+CAPB mixtures is studied. It is shown that the cosurfactants with 8 and 10 carbon atoms in their hydrophobic tail and with small nonionic head group (-OH and -COOH) are able not only to increase significantly the viscosity of the concentrated surfactant solutions (10 wt%), but also to increase significantly the rate of surfactant adsorption for diluted solutions (0.5 wt%). The later effect is explained with the mismatch of the chain-lengths of the main surfactants and the cosurfactant. This mismatch leads to faster release of the surfactant molecules from the mixed surfactant+cosurfactant micelles. The increase of the cosurfactant head-group size leads to much smaller effect on the rate of surfactant adsorption, due to the lower affinity of these molecules to be incorporated in the surfactant micelles. The addition of cationic cosurfactants with appropriate chain length (C8 or C10) has also very significant impact on both the viscosity of the concentrated solutions and dynamic surface tension of the diluted solutions, due to the strong electrostatic attraction of the cosurfactant molecules with those of the main anionic surfactant.

We observe a strong correlation between the viscosity of the concentrated solutions and the dynamic surface tension of the diluted solutions for all SLES+CAPB+cosurfactant mixtures. Highly viscous concentrated solutions containing WLM correspond to diluted solutions with much faster surfactant adsorption kinetics.

The equilibrium surface tension decreases with increasing the chain length of the cosurfactant and with decreasing the head-group size for cationic and nonionic cosurfactants. This effect is explained with the formation of denser adsorption layer when long-chain cosurfactants with small head-group are added in the system. The equilibrium surface tension of the basic surfactant solution is affected very weakly by the addition of anionic cosurfactants, because these cosurfactants are not incorporated in the adsorption layer, due to their electrostatic repulsion with the SLES molecules.

These results and conclusions can be used for selecting appropriate cosurfactants and for rational design of viscous concentrated surfactant formulations for home and personal care, which exhibit also appropriate adsorption properties upon application when often dilution takes place.

CRediT authorship contribution statement

Zlatina Mitrinova: Investigation, Formal analysis, Visualization, Writing – original draft. **Maria Chenkova:** Investigation, Formal analysis. **Nikolai Denkov:** Conceptualization, Methodology, Writing – review & editing. **Slavka Tcholakova:** Conceptualization, Methodology, Formal analysis, Writing – review & editing, Supervision.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2022.129221.

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