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# Colloids and Surfaces A: Physicochemical and Engineering Aspects

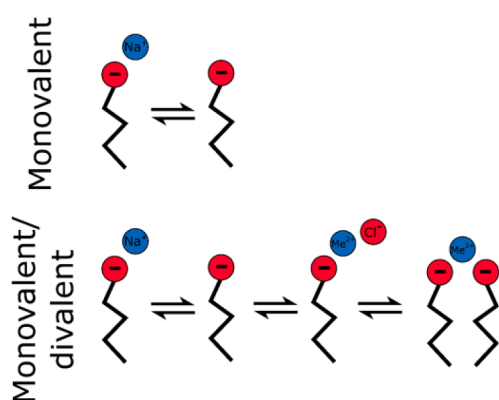
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## The influence of divalent cations on the dynamic surface tension of sodium dodecylbenzenesulfonate solutions

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### GRAPHICAL ABSTRACT



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### ABSTRACT

The kinetics of surfactant adsorption at interfaces is crucial in many industrial settings. Maximum bubble pressure tensiometry allows accessing the adsorption at time scales of tens of ms to uncover the initial stages of surfactant diffusion to the interface. This method was used to investigate electrolyte solutions of sodium dodecylbenzenesulfonate (SDBS), specifically targeting how the presence of small amounts of divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ ) influenced the adsorption kinetics and equilibrium. The dynamic surface tensions revealed that the adsorption of SDBS was strongly influenced by the presence of divalent cations due to strong interactions with the anionic surfactant. In addition, the type (i.e. size) of cations played a role. The strong divalent cation-surfactant interactions lead to distinct lowering of surfactant diffusion coefficients, calculated using the short-time approximation solution of the Ward-Tordai equation. The diffusion coefficients were slightly and similarly lowered for all types of divalent cations when the surfactant concentration was increased up to the critical micelle concentration (CMC). Above CMC, the diffusion coefficients increased steadily depending on the divalent cation. It was speculated that this could be due to differences in structure and aggregation numbers of micelles and slower disassembly of micelles to supply monomers for adsorption. Furthermore, CMC of SDBS was reduced according to the Hofmeister series in the presence of divalent cations.

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## 1. Introduction

The adsorption kinetics of surfactants at fluid interfaces is of importance in many technical, biological and industrial applications, including wetting, detergency, foaming, emulsification, separation and ion flotation [1–6]. The adsorption is typically investigated by measuring the dynamic surface tension of newly created interfaces exposed to surfactant solutions. Measurements of the surfactant dynamics can be performed at time scales down to milliseconds with the maximum bubble pressure technique. The occurrence of commercial and reliable maximum bubble pressure instruments was initially accompanied with studies that developed theoretical and experimental approaches to follow the adsorption kinetics [7–12]. Subsequently, the method has been used to investigate the adsorption behaviour of bio-surfactants [13,14], gemini surfactants [15], mixed surfactant solutions [16], lung surfactants interacting with inhalable powders [17] and fragrance molecules [18].

The short time adsorption kinetics of ionic surfactants at air-water interfaces have been investigated to some extent. A series of sodium alkyl sulphates were used by Fainerman et al. to analyse the adsorption kinetics in terms of their asymptotic solutions of the adsorption kinetic theory [7]. Subsequently, they followed the adsorption behaviour of sulphate and sulphonate based surfactants with various extents of ethoxylation in the structure [19]. Gao et al. investigated the adsorption kinetics of sulfosuccinate surfactants [20], Kalekar et al. looked at how various organic additives affected the dynamic behaviour of sodium lauryl sulphate [21], while the adsorption kinetics of mixed anionic-cationic (sodium dodecyl sulphate and dodecyl-trimethylammonium bromide) surfactant solutions was followed by Frese et al. [16]. In all these studies pure water was the solvent, and the structure and concentration of surfactants were the prime interest.

Despite the influence of electrolytes on the adsorption kinetics and their presence in most technical systems and applications. Ritacco et al. used addition of sodium bromide to probe the influence of electrostatics on the adsorption kinetics of dodecyl trimethylammonium bromide [22]. The adsorption kinetics of sodium dodecyl sulphate and dodecyl trimethylammonium bromide in various monovalent salt solutions were studied by Danov et al. to verify theoretically derived expressions which showed that the diffusivity of ionic surfactants largely depended on the concentration of surfactant and non-amphiphilic salt [23]. Even though traces of divalent cations significantly influenced the adsorption of various sulfonate surfactants at oil-water interfaces [24,25], to the best of our knowledge, no studies have reported on how the presence of divalent cations influence the short-time adsorption kinetics of anionic surfactants at air-water interfaces.

The purpose of this study was to investigate how the presence of small amounts of divalent cations in sodium chloride solutions influenced the adsorption behaviour of sodium dodecylbenzenesulfonate (SDBS) at the air-water interface. The divalent cations were  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$ . Dynamic surface tension measurements were performed using the maximum bubble pressure method with bubble lifetimes ranging from milliseconds to minutes. The dynamic surface tension profiles were analysed in terms of the short-time approximations of the Ward-Tordai equation for surfactant adsorption. The resulting diffusion coefficients were used to estimate the time span of diffusion limited adsorption for the various surfactant systems. The surface tension at the longest bubble lifetimes ( $> 100$  s) were used to estimate the critical micelle concentration (CMC) and evaluate thermodynamic parameters.

## 2. Experimental

### 2.1. Chemicals

The surfactant used in this study was sodium dodecylbenzenesulfonate (Sigma-Aldrich, technical grade). The salts were NaCl (Merck Emsure, p.a.),  $CaCl_2 \cdot 2H_2O$  (Sigma-Aldrich, p.a.),  $MgCl_2 \cdot 6H_2O$  (Merck, p.

a.),  $BaCl_2 \cdot 2H_2O$  (Riedel-de-Haën, p.a.),  $SrCl_2 \cdot 6H_2O$  (Sigma-Aldrich, 99%). All the chemicals were used as received. Ion exchanged water with resistivity  $18.2 M\Omega cm^{-1}$  (Millipore Simplicity System) was used to prepare all the solutions.

### 2.2. Aqueous solutions

Stock solutions of SDBS were prepared by dissolving the surfactant in the appropriate electrolyte solution. The ionic composition in the electrolyte solutions consisted of pure sodium chloride or sodium chloride mixed with small amount of either calcium, magnesium, barium or strontium chloride. Two molar ratios (117 and 57) between monovalent and divalent cations were used, while the ionic strength was always kept constant at 20 mM. The stock solutions were diluted with the appropriate electrolyte solutions to give surfactant concentrations from well above to well below the critical micelle concentrations. Some issues with solubility were encountered at the highest concentrations of barium and strontium, and precipitates might have formed. Similar observations were made with the same series of divalent ions in a study of the solubility of dodecyl sulfate salts [26].

### 2.3. Density measurements

The density of the aqueous solutions was measured at 25 °C using a density meter (DMH 5000, Anton Paar, Austria). The values were used as an input parameter in the surface tension measurements.

### 2.4. Dynamic surface tension measurements

The dynamic surface tension was measured with a maximum bubble pressure tensiometer (BP100, Krüss, Germany). A hydrophobized glass capillary (SH3120, Krüss, Germany) with inner diameter of approximately 0.2 mm was immersed into 35 ml aqueous solutions. Air bubbles with surface ages from about 10 ms to 250 s were formed in the solution and the surface tension was obtained from the maximum pressure measurements using the Young-Laplace equation. The surface tension of deionized water (from a Millipore Simplicity System) was within  $72 \pm 1$  mN/m before any sample measurements were started. All the measurements were carried out at  $25 \pm 1$  °C. Three repeated measurements were performed for all solutions.

### 2.5. Data analysis

#### 2.5.1. Equilibrium surface tension analysis

For most of the systems, equilibrium surface tensions were reached during the last measurement points, i.e. surface ages from 160 to 250 s (Fig. S1 in Supporting Information). The equilibrium values were calculated as the average of these measurements and the standard deviation was less than 0.6 mN/m in all cases. For both solutions with of barium and the solutions with the highest amount of magnesium and strontium, there was still a minor decay in surface tension when the surface age increased from 200 to 250 s (Fig. S2 in Supporting Information). However, the change was small and the values measured at these two surface ages were used as the equilibrium surface tension. The standard deviation was less than 0.9 mN/m.

The critical micelle concentrations (CMC) were determined from the break point in the curves when equilibrium surface tensions were plotted against the logarithms of surfactant concentrations (Fig. S3 in Supporting Information). One linear regression was carried out for the points where the surface tension clearly changed, while a second linear regression was carried out for the points with virtually no change in the surface tension. The CMC values were calculated by equating the two equations and solving for  $\log [SDBS]$ .

The surface excess ( $\Gamma_{max}$ ) and minimum surface area per surfactant ( $A_{min}$ ) were calculated using Gibbs adsorption isotherm:

**Table 1**

Literature values [39–44] for SDBS properties in pure water.

Property	
CMC (mM)	1.20–3.00
$N_{agg}$	51–62
$\Gamma_{max}$ ( $10^6$ mol/m <sup>2</sup> )	1.62
$A_{min}$ ( $\text{\AA}^2$ /molecule)	103
$\Delta G_{ads}^0$ (kJ/mol)	-57.1
$\Delta G_{mic}^0$ (kJ/mol)	-31.5
$\Delta G_{ads}^0/\Delta G_{mic}^0$	1.8

$$\Gamma_{max} = \frac{1}{2.303nRT} \left( \frac{d\gamma}{d\log c} \right) = \frac{1}{A_{min} N_A} \quad (1)$$

where  $\left( \frac{d\gamma}{d\log c} \right)$  is the slope describing the change in surface tension ( $\gamma$ ) as a function of the bulk surfactant concentration ( $c$ ) below CMC,  $R$  is the gas constant,  $T$  is the temperature in Kelvin,  $n$  is a constant depending on the number of components the surfactant consists of and  $N_A$  is Avogadro's number. In this study, the calculations were performed with  $n = 1$  since the electrolyte concentrations were considerably higher than the surfactant concentrations.

The standard free energy of micellisation ( $\Delta G_{mic}^0$ ) was calculated by the following equation:

$$\Delta G_{mic}^0 = RT \ln(cmc) \quad (2)$$

The standard free energy of adsorption at the air-solution interface ( $\Delta G_{ads}^0$ ) was calculated by the following equation:

$$\Delta G_{ads}^0 = \Delta G_{mic}^0 - \frac{\pi}{\Gamma_{max}} \quad (3)$$

where  $\pi$  is the surface pressure,  $\gamma_0 - \gamma_{eq}$ , with  $\gamma_0$  and  $\gamma_{eq}$  representing the surface tension of pure aqueous solution and equilibrium surface tension, respectively.

### 2.5.2. Dynamic surface tension analysis

Two models are usually used to describe transport and adsorption of surfactant monomers to an interface [27]:

1. The diffusion-controlled mechanism. Here a region of the bulk solution close to the surface, a few molecular diameters thick, is defined as the “sub-surface”. The monomers diffuse from the bulk solution and into the sub-surface region. Once the monomers are in the sub-surface region, it is assumed that they adsorb instantaneously onto the interface. This means that the rate-determining step is the diffusion from the bulk solution to the sub-surface.
2. The mixed kinetic-diffusion mechanism. Also in this model, the monomers diffuse from the bulk solution and into the sub-surface. However, here it is assumed that an adsorption barrier prevents instantaneous adsorption when the monomers enter the sub-surface region. The rate-determining step in this case is the transfer of monomers from the sub-surface to the interface. The adsorption

barrier can be due to various factors that can decrease the adsorption rate, including increased surface pressure as the surface fills up or charge, steric or orientation restraints that slow down adsorption of molecules to the interface. The result will be diffusion of molecules back to the bulk solution and increased time for the decay in the interfacial tension.

The starting point for evaluating adsorption mechanisms is often to consider deviations from the purely diffusion-controlled mechanism [27]. The classical Ward-Tordai equation describes the adsorption of surfactants on a clean surface as a purely diffusion-controlled process [28]:

$$\Gamma(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} - 2\sqrt{\frac{D}{\pi}} \int_0^t c_s(t-\tau) d\tau^{1/2} \quad (4)$$

where  $\Gamma(t)$  is the surface excess at time  $t$ ,  $c_0$  is the bulk surfactant concentration,  $D$  is the surfactant diffusion coefficient,  $c_s$  is the surfactant concentration in the sub-surface and  $\tau$  is a dummy variable of integration. The first term in this equation accounts for the diffusion of surfactants from the bulk to the interface, while the second term accounts for diffusion back to the bulk when the interface becomes sufficiently crowded. In most cases the equation cannot be solved analytically, but asymptotic solutions have been derived [7].

Since no back diffusion will occur at the beginning of the adsorption process, the last term of Eq. 4 can be neglected. The surface excess can then be approximated by the following equation:

$$\Gamma(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} \quad (5)$$

An appropriate adsorption isotherm is required to relate  $\Gamma(t)$  and the dynamic surface tension,  $\gamma(t)$ . The surfactant solution is dilute at the beginning of the adsorption (i.e.  $\gamma \rightarrow \gamma_0$ ) and the linear Henry isotherm can be used:

$$\gamma - \gamma_0 = -nRT\Gamma \quad (6)$$

where  $n$  was set equal to one because the electrolyte concentration was considerably higher than the surfactant concentrations in the solutions. Substitution of Eq. 6 into Eq. 5 results in the following:

$$\gamma_{t \rightarrow 0} = \gamma_0 - 2RTc_0 \sqrt{\frac{Dt}{\pi}} \quad (7)$$

The dynamic surface tension data was used to make plots of  $\gamma$  versus  $\sqrt{t}$  (Fig. S4 in Supporting Information), and the diffusion coefficients ( $D$ ) were calculated in the linear (i.e. diffusion controlled) region using Eq. 7.

## 3. Results and discussion

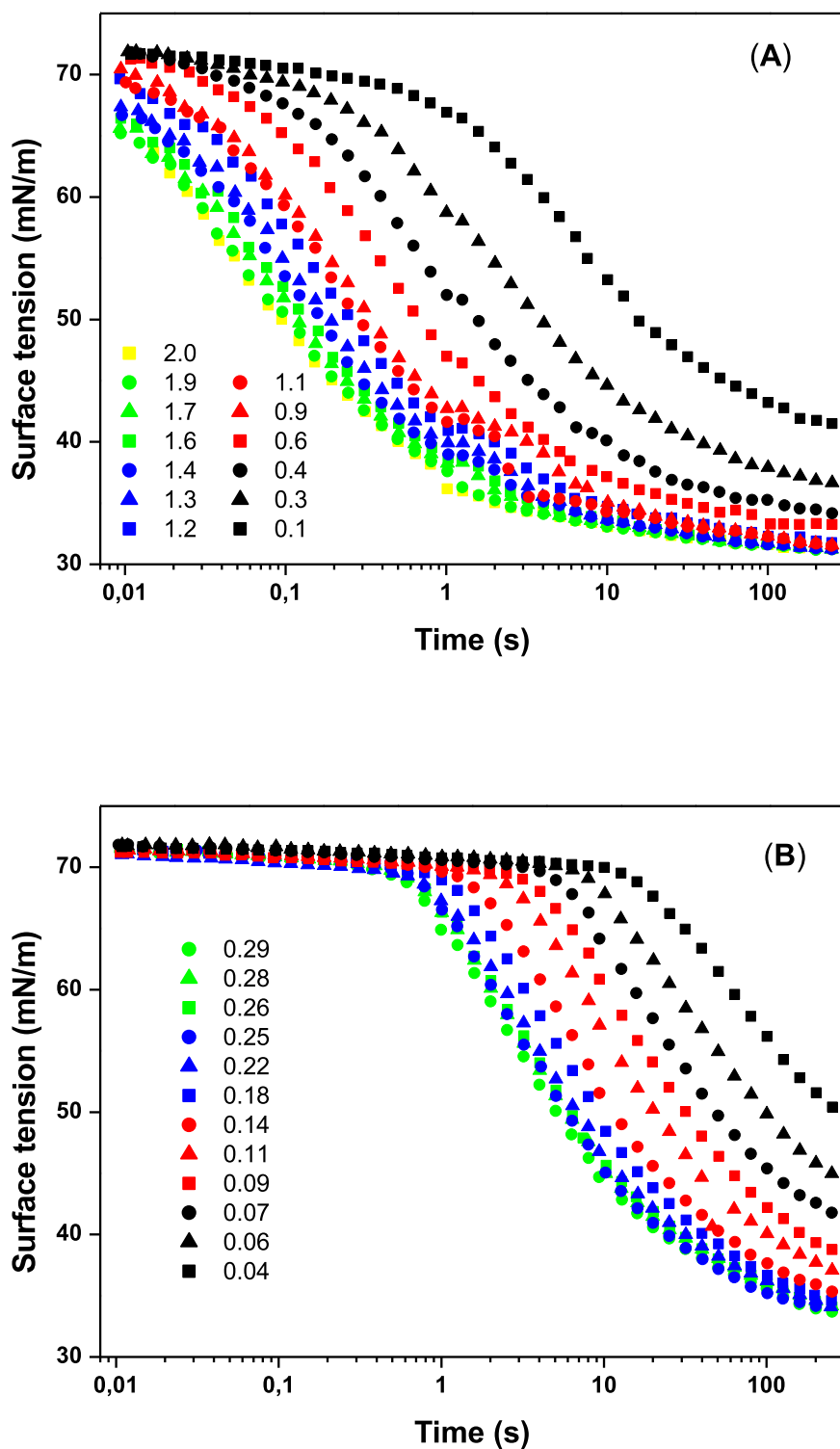
### 3.1. Equilibrium surface tensions

Table 1 lists values from the literature for the critical micelle concentration, average number of surfactants in micelles ( $N_{agg}$ ), surface

**Table 2**

Parameters calculated from the equilibrium surface tension.

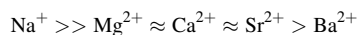
Sample	CMC (mM)	$\gamma_{beyond-CMC}$ (mN/m)	$\Gamma_{max}$ ( $10^6$ mol/m <sup>2</sup> )	$A_{min}$ ( $\text{\AA}^2$ /molecule)	$\Delta G_{ads}^0$ (kJ/mol)	$\Delta G_{mic}^0$ (kJ/mol)	$\Delta G_{ads}^0/\Delta G_{mic}^0$
Pure NaCl	0.67±0.04	31.9±0.3	2.45±0.49	68±4	-34.2±1.1	-18.1±0.1	1.9
Na/Mg= 117	0.35±0.02	30.8±0.2	3.46±0.20	48±3	-31.4±0.6	-19.7±0.2	1.6
Na/Mg= 57	0.31±0.04	29.5±1.3	4.54±0.84	37±7	-29.5±1.1	-20.1±0.4	1.5
Na/Ca= 117	0.37±0.03	29.5±0.2	3.30±0.62	52±11	-32.5±2.9	-19.6±0.2	1.7
Na/Ca= 57	0.30±0.01	28.0±0.0	3.32±0.18	50±3	-33.2±0.6	-20.1±0.1	1.7
Na/Sr= 117	0.37±0.01	29.4±0.6	3.82±0.57	44±7	-30.7±1.7	-19.6±0.1	1.6
Na/Sr= 57	0.24±0.02	29.9±0.1	5.00±0.22	33±2	-29.0±0.3	-20.7±0.2	1.4
Na/Ba117	0.20±0.04	31.6±1.0	3.38±0.58	50±8	-33.2±2.4	-21.2±0.5	1.6
Na/Ba= 57	0.16±0.03	34.6±0.2	3.51±0.41	48±6	-34.1±3.0	-21.7±0.5	1.6



**Fig. 1.** : The dynamic surface tension on logarithmic time scale of SDBS in (A) NaCl solutions and (B) mixed NaCl and BaCl<sub>2</sub> solutions (molar ratio Na/Ba = 57), both at ionic strength 20 mM. The legends indicate the surfactant concentrations (mM).

excess, minimum surface area per surfactant and Gibbs free energy of adsorption and micellization for SDBS in pure water. The properties calculated from the equilibrium surface tensions in this study are listed in Table 2. Dissolved in 20 mM sodium chloride solution, the CMC of SDBS was 0.67 mM. This is lower than the CMC values reported for pure water, which range from 1.20 to 3.00 mM. The lower value is reasonable since the presence of electrolyte will screen the repulsion between negatively charged sulfonate groups and thereby promote micelle

formation. The presence of divalent cations lowered the CMC values further, and the largest reduction was observed for the solutions with the highest amounts of divalent cations. The sequence of CMC values for the solutions with lowest amounts of divalent cations (i.e. Na/X = 117, where X is the divalent cation) was as follows:



Here, the solutions with barium had notably lower CMC than the

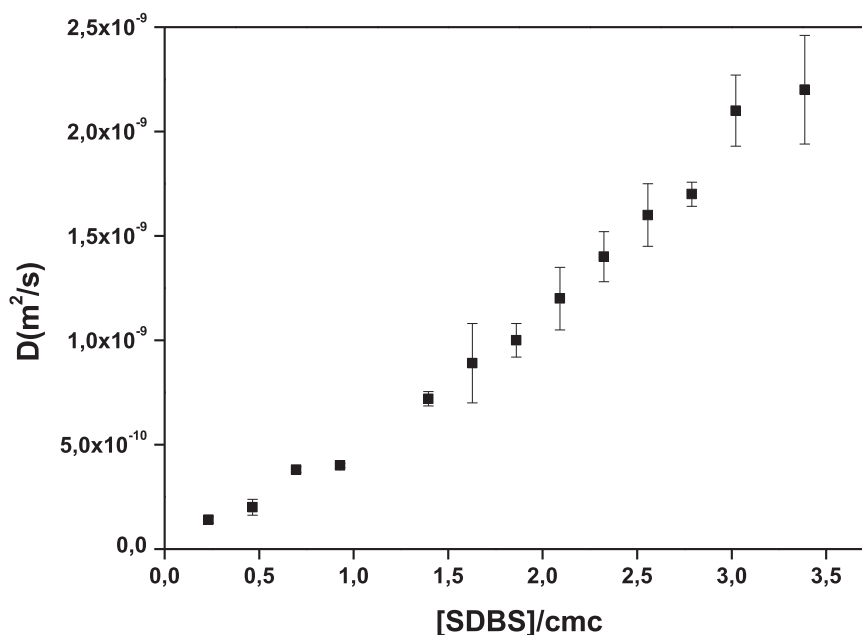


Fig. 2. : The diffusion coefficients for SDBS in NaCl solutions at ionic strength 20 mM.

other solutions with divalent ions. At the high amounts of divalent cations ( $\text{Na}/X = 57$ ), the sequence changed into the following:



In this case, both strontium and barium solutions showed lower CMC compared to the other two ions, still with a markedly lower value for the barium solutions. In summary, the amount and type of divalent cations affected the CMC of the surfactant solutions, which means that the divalent cations interacted stronger with the sulfonate headgroups of the surfactant than the monovalent sodium ions. This agrees with other studies as well [24,29–31]. Furthermore, the effect of the ions followed a Hofmeister series, i.e. the CMC values became lower when the ion-size of the divalent ions increased. Sulfonates have been classified as large anionic headgroups [32], and the trend indicated that they interacted preferentially with the largest counterions. This is consistent with empirical observations of matching water affinities for simple electrolytes, where large cations preferentially interact with large anions [33].

None of the other properties based on the equilibrium surface tensions showed the same Hofmeister sequence. The surface tensions beyond CMC were slightly lower in the presence of divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ ) than in the sodium chloride solution. This indicated closer packing of the surfactants at the interface at constant ionic strength of the solutions. In the solutions containing  $\text{Ba}^{2+}$ , however, the surface tension was higher than in the pure sodium chloride solution. This could be a result of the strong interactions between barium and sulfonate groups promoting formation of complexes with two surfactant molecules attached to one barium ion. Such complexes could have lower solubility than for the other metal ions and precipitate in the solutions [34]. This would appear as reduced interfacial activity.

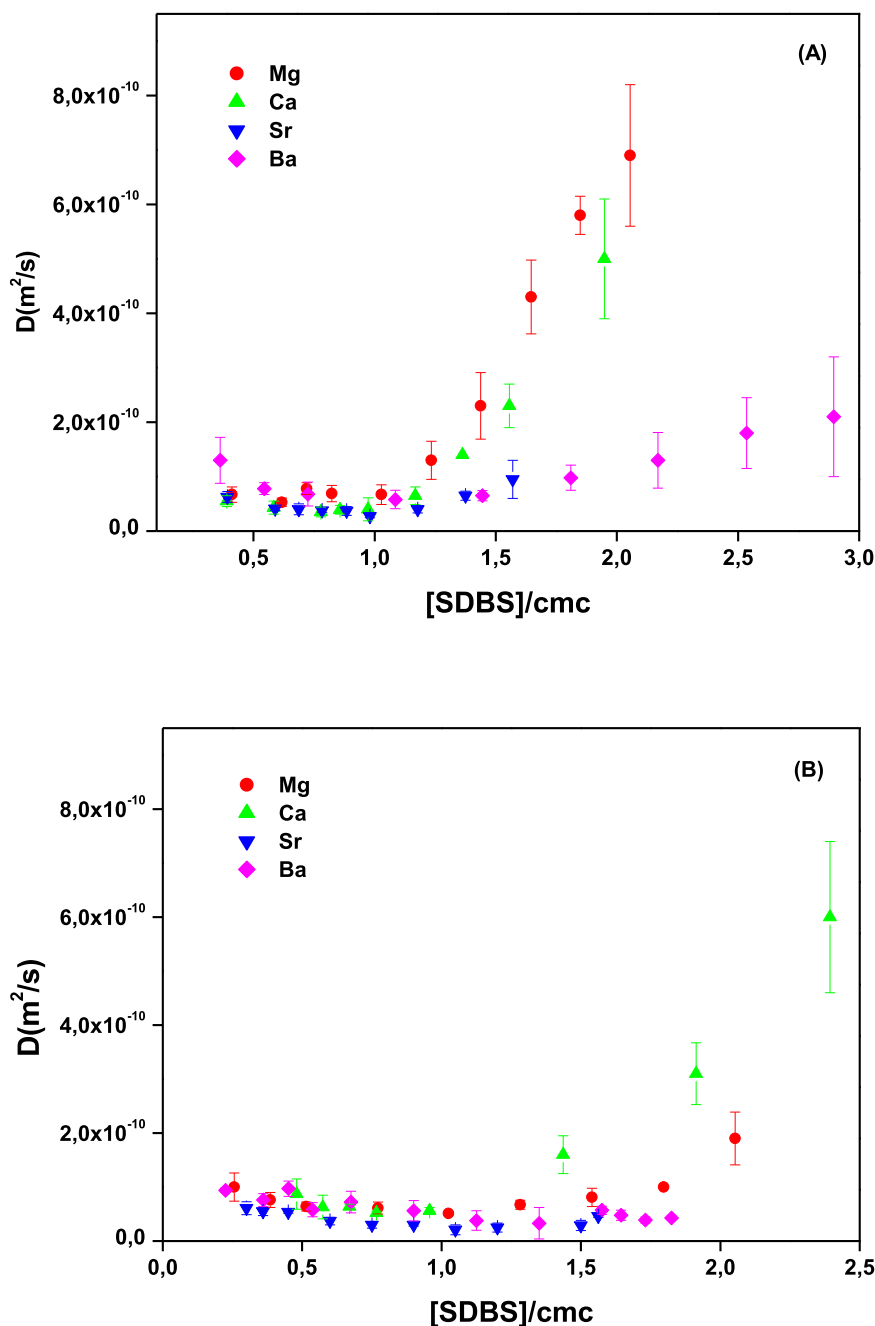
The surface excess was considerably higher in the electrolyte solutions (Table 2) than in pure water (Table 1), again demonstrating the charge screening effect by the cations, resulting in closer packing of surfactants at the interface. The strong interactions between the divalent ions and surfactant increased the surface excess and surfactant packing further, with most pronounced effect at high amounts of  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$ . The corresponding molecular areas showed a change from 103 Å<sup>2</sup>/molecule in pure water to 68 Å<sup>2</sup>/molecule in pure sodium chloride, while the average values ranged from 44 to 52 Å<sup>2</sup>/molecule and from 33 to 50 Å<sup>2</sup>/molecule for the lowest and highest amounts of divalent ions, respectively.

The change in Gibbs free energy of both adsorption and micellization became significantly smaller in electrolyte solutions, compared to pure water. The ratio between free energy of adsorption and free energy of micellization was, however, similar in pure water (1.8) and 20 mM NaCl (1.9). In the presence of divalent cations, this ratio was somewhat lower (1.4–1.7). The free energy of adsorption increased somewhat in the presence of divalent cations (Table 2). This was accompanied by a decrease in the free energy of micellization, showing that the divalent ions promoted micelle formation, in agreement with the lowering of the CMC values. Nevertheless, the free energy of adsorption was considerably lower than the free energy of micellization, and in all the systems the surfactant showed higher preference for adsorbing at the interface than forming micelles. This is also reflected in relatively low aggregation numbers, ranging from 51 to 62 in pure water (Table 1) and 59 in 10 mM NaCl [35].

### 3.2. Dynamic surface tensions

The dynamic surface tensions for SDBS dissolved in sodium chloride solutions with and without  $\text{Ba}^{2+}$  present are shown in Fig. 1. The logarithmic time scale emphasizes the effects of surfactant concentration at the short surface ages. Clearly, the surface tensions decreased more rapidly in the pure sodium chloride solutions than in the presence of barium ions. Furthermore, the surface tension decreased more rapidly when the surfactant concentrations increased, Fig. 1A. For the most concentrated surfactant solutions a notable decay in the surface tension occurred already after 10 ms, while it occurred around 100 ms for the most dilute solutions. Increased surfactant concentration also resulted in faster reduction of the surface tension in the systems with barium present, Fig. 1B. In this case, however, it took about 1 s for the most concentrated surfactant solutions and around 10 s for the most dilute surfactant solutions before significant reduction in the surface tension was observed. Generally, the presence of divalent ions slowed down the adsorption kinetics considerably, and the two systems shown here represented the most pronounced difference. The remaining surface tension curves can be found in the Supporting Information (Fig. S5).

The diffusion coefficients, calculated in the diffusion-controlled regime, for the different SDBS concentrations in pure NaCl solutions are plotted in Fig. 2. Below CMC, the diffusion coefficient increased from  $1.4 - 4.0 \times 10^{-10} \text{ m}^2/\text{s}$  with increasing concentration. Literature values



**Fig. 3.** : The diffusion coefficient for SDBS in salt solutions at ionic strength 20 mM with the molar ratio  $\text{Na}/\text{X} = 117$  (A) and  $\text{Na}/\text{X} = 57$  (B), where X is the divalent ion.

for the diffusion coefficients of SDBS were not found, but diffusion coefficients reported for sodium dodecyl sulfate (SDS), a relatively similar anionic surfactant, are in the range  $7.9 - 11.2 \times 10^{-10} \text{ m}^2/\text{s}$  [36,37]. Considering that the molecular weight for SDBS is higher (348.5 g/mol) than for SDS (288.4 g/mol), the values calculated for SDBS were reasonable. Above CMC, the diffusion coefficients increased faster with concentration than below it and reached  $2.2 \times 10^{-9} \text{ m}^2/\text{s}$  at 3.4 CMC.

The diffusion coefficients were lower in the presence of divalent ions and demonstrated effective interactions between the sulfonate head-groups of surfactant monomers and the divalent cations as discussed above. The evolution of diffusion coefficients was also different with divalent ions present, Fig. 3. Below CMC, the diffusion coefficient slightly declined with increasing SDBS content for both ratios of divalent ions. The decline was from  $1.3 \times 10^{-10} - 2.7 \times 10^{-11} \text{ m}^2/\text{s}$  at low

amounts of divalent ions and from  $1.0 \times 10^{-10} - 3.0 \times 10^{-11} \text{ m}^2/\text{s}$  at high amounts of divalent ions. Beyond CMC, the diffusion coefficients increased depending on the type and amounts of divalent ions. For the lowest amount of divalent cations, the diffusion coefficient increased fastest for magnesium and calcium, reaching  $6.9 \times 10^{-10} \text{ m}^2/\text{s}$  at about 2 CMC, while it was slower for strontium and barium, where the latter reached  $2.1 \times 10^{-10} \text{ m}^2/\text{s}$  at about 3 CMC (Fig. 3A). The trends were similar, but the diffusion coefficient increased slower at the highest amounts of divalent ions (Fig. 3B).

The results above will initially be discussed for surfactant concentrations below CMC, followed by a discussion for concentrations above CMC.

In the solutions below CMC with only monovalent cations, the surfactant molecules will be present both in a non-dissociated and



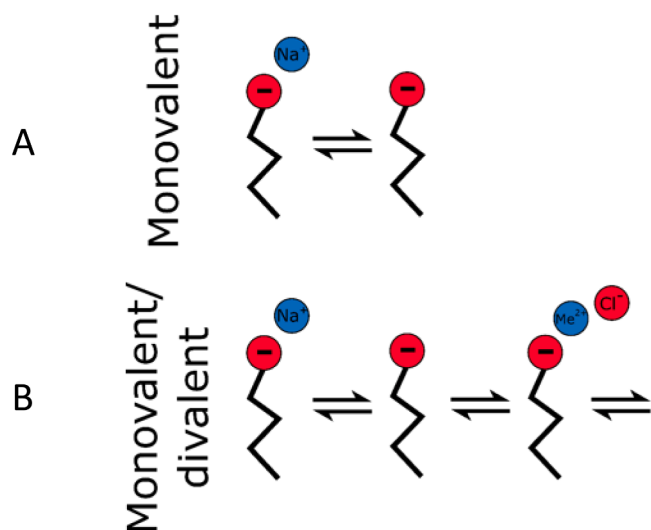


Fig. 4. : Dissociation and complex formation of surfactant in solutions with monovalent counterions (A) and mixtures of monovalent and divalent counterions (B).

dissociated form, Fig. 4A. Increasing the concentration of the surfactant will lead to increased chemical potential gradients between the bulk solution and the sub-surface layer, which will be the driving force for the diffusion to the sub-surface and adsorption of surfactants at the air-water interface.

In the solutions with both mono- and divalent cations, the overall lowering of the values of the diffusion coefficients demonstrate surfactant-divalent cation interactions. Now additional surfactant-ion configurations can occur: i) complexes between a dissociated surfactant, a divalent cation, and a chloride anion, and ii) complexes between two dissociated surfactants and a divalent cation, Fig. 4B. These complexes will become more prevalent in the solutions as the surfactant concentration approaches CMC, and since their molecular weights are larger than for both the dissociated and undissociated SDBS it can explain the slight decrease in the diffusion coefficients when the surfactant concentration approached CMC (and even beyond CMC for the Na/X = 57 solutions).

Above CMC, the increase in diffusion coefficients with increasing surfactant concentration for the lowest amounts of divalent ions (Fig. 3A) can be considered in view of the one-to-one stoichiometry between the surfactants and divalent cations. Beyond this stoichiometric concentration, all the divalent ions are consumed and the amount of undissociated and dissociated surfactants will increase in the solutions, resulting in faster diffusion and higher diffusion coefficients. For solutions containing magnesium, calcium and strontium the stoichiometric concentrations are in the same range as the corresponding CMCs and agreed well with the concentration where the diffusion coefficients started to increase. For the solutions containing barium, the one-to-one stoichiometry occurred at a surfactant concentration considerably higher than the CMC, and in this case the increase in diffusion coefficient values started at higher concentrations and was less pronounced. For the solutions with the high amounts of divalent ions (Na/X = 57), however, the one-to-one stoichiometry between the surfactants and divalent cations are at surfactant concentrations 2–3 times the CMC. Even though the diffusion coefficients were quite similar for all solutions up to about 1.5 times CMC, they started to increase already at this concentration for the solutions with magnesium and calcium. This suggested that other factors also influenced the diffusion process.

Disassembly of micelles will provide surfactant monomers that diffuse into the subsurface and become adsorbed at the bubble surface. In the solutions with pure sodium chloride, the micellar disassembly kinetics was likely fast enough to supply monomers for the diffusion

process. In the solutions with divalent cations, however, the stronger interactions between counterions and surfactant molecules probably slowed down the disassembly kinetics. Furthermore, it has been reported that the aggregation number of sodium dodecyl sulfate, a similar surfactant to SDBS, changed from ca. 60 in monovalent ion solutions to up to 100, depending on the type of divalent counterions [38]. It is reasonable to assume similar trends for SDBS, and that there can be a transition from spherical to more rod-like micelle shapes upon adding the divalent cations. Hence, they would not only slow down the disassembly kinetics, but also slow down the diffusion of micelles (i.e. monomer reservoirs) towards the subsurface.

#### 4. Conclusions

The adsorption kinetics of SDBS at short time scales and micelle formation were shown to be largely dependent on the concentration and type of divalent cations present in the solutions. Both equilibrium and kinetic analyses showed that the monovalent sodium ions could be replaced by divalent cations through strong interactions with the anionic surfactant. The CMC of the solutions decreased according to the Hofmeister series, while other properties, like surface excess and molecular area, did not strictly follow this trend. The dynamic surface tension analysis revealed stark differences in the initial stages of the SDBS-cation complexes diffusion to the air-water interfaces. In the systems with only sodium, the diffusion coefficients continuously increased with increasing surfactant concentration. In the presence of divalent cations, the diffusion coefficients decreased slightly up to a certain concentration (close to or somewhat beyond the CMC). This behaviour can be attributed to formation of larger divalent cation – surfactant complexes below CMC, and retarded micellar disassembly kinetics and transitions into larger micelle aggregates above CMC.

#### CRedit authorship contribution statement

**Marcin Dudek:** Conceptualization, Methodology, Formal analysis, Investigation, Writing, Supervision. **Arnt Ove Jektvik:** Methodology, Formal analysis, Investigation. **Gisle Øye:** Conceptualization, Formal analysis, Writing, Supervision, Funding acquisition.

#### Declaration of Competing Interest

We declare no conflicts of interest.

#### Data Availability

Data will be made available on request.

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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.2023.132007](https://doi.org/10.1016/j.colsurfa.2023.132007).

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