

## Ion-specific effects on foam films and foam from diluted solution of sodium dodecyl sulfate

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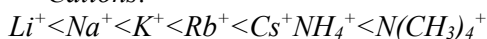
The ion-specific effects on extremely diluted solutions of surfactants are poorly studied. The effect of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> ions on the properties of foam films and foam stabilized by 0.05 mmol/L sodium dodecyl sulfate (SDS) was studied. Each one of the salts LiCl, NaCl and KCl in the concentration range of 1.1 mmol/L to 50 mmol/L was added to 0.05 mmol/L solution of SDS, for studying the properties of its foam films and foams. It was established that the surface potential of the foam films does not depend on the type of salt added, which means that no ion-specific effects are registered. On the contrary, such effects are evident in the case of foam produced by sparging of gas through porous bottom of column containing the same solutions. Thus, the rates of foaming, foam decay and the foam lifetime vs. the concentration of added salt (LiCl, NaCl and KCl) were studied by means of Dynamic Foam Analyzer (DFA-100, Kruss Ltd, Germany). The foam production number for each one of these cases was calculated as well. It was established that both NaCl and KCl boost the foam, the first one of which being stronger than the second one. On the contrary, LiCl has no effect on the foamability of the system. The present study is an example for manifestation of a salt-specific effect under dynamic conditions, which vanishes under static conditions.

**Keywords:** ion-specific effects, foam films, foam, adsorption layer, surfactant

### INTRODUCTION

It has been established since long time ago that different salts differently affect the physico-chemical properties of solvents, solutes, dispersed systems and biological cells. For example, Ostwald [1] reported that the vapor pressure of the solvent weakly depends on the type of the added salt. Raoult [2] had similar observation for the freezing points of the solutes in presence of different salts. De Vries [3] explored the specific effect of different salts on live plant cells and established that there exist a certain concentration specific for each salt, at which the protoplasm of the cell peels away from the cell wall (plasmolysis). The same effect has been confirmed by Hamburger [4] for the red blood cells. Hofmeister [5-7] established that the blood proteins salt out at a certain concentration specific for each salt. He succeeded to separate the effects of the anions and those of the salts and ordered them in the following series of increasing strength for precipitation of the blood proteins:

*Cations:*



*Anions:*



The effect of the anions has been found to be stronger than that of the cations. Significantly later

on, the same systems were explored by means of small-angle X-ray scattering (SAXS) [8]. Thus, it was established that the addition of salt generally initiates attraction between the protein molecules, but with a power specific for each salt [8, 9]. Surprisingly, it was found out that some salts have the ability to slow down the coalescence of bubbles in aqueous medium at a certain specific concentration, while other salts do not have such an effect [10, 11]. The same observations were made on aqueous foam films [12, 13]. Recent studies on the effect of co-ions [14-16] and counter-ions [17, 18] on the properties of foam, wetting and emulsion films indicated a specific adsorption of the ions on the interface boundaries depending on their specific energy of adsorption, sizes and hydration shells, thus affecting the surface potentials of the interface boundaries. The higher the value of the specific adsorption energy of the ion, the larger is its adsorption on the film surfaces. Hence, counter-ions with larger specific adsorption energy should contribute for thinner films and less stable dispersed systems and *vice versa*. Indeed, our theoretical expectations regarding the thickness of the thin films are fulfilled [14-18], but the experiments on foam's and emulsion's stability show the opposite effect – counter-ions with larger specific energy of adsorption contribute for more stable foams and

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emulsions [17, 19, 20]. The systems, which have been studied in these cases contain ionic surfactants with concentrations close to  $C/CMC \approx 1/2$ . It is not clear if the ion-specific effect will be manifested at more diluted surfactant solutions (e.g.  $C/CMC \approx 0.05$ ). For this reason, we explored the effect of LiCl, NaCl and KCl on the properties of foam films and foam stabilized by 0.05 mmol/L SDS.

## EXPERIMENTAL

### *Interferometric study of foam films*

The interferometric method for studying thin liquid films allows one to calculate the surface potential of the film surfaces [21]. The setup consists of two units: (i) the cell in which the film is formed, and (ii) the optic-electronic system for monitoring the film and registration of its interferometric image.

The cell contains a film holder with radius of 2.15 mm, which has an orifice aside, connected to a capillary tube and a mercury pump. The film holder is dipped into the surfactant solution and pulled out, thus forming a double concave drop. After this the two tips of the double concave drop are approached toward each other by gentle suction of the liquid using the mercury pump until the formation of the foam film. Immediately after its formation, it starts draining due to the action of the capillary pressure. The foam film is vertically illuminated with a beam of coherent monochromatic light ( $\lambda = 551$  nm) generated by an inverted microscope (Carl Zeiss, Germany) and reflected by the two surfaces of the film, thus causing the appearance of two phase-shifted beams of reflected light, which are collected together and captured by a Sony – SSC-M388CE photo-camera as a temporal general interferogram. The latter one is recorded on computer as a movie in “avi” format. “Image J” software is used for processing the movie. Hence, the movie of the evolution of the general interferogram is split to pictures in a 0.083 seconds-time frame. The software extracts the signal from a small spot on the general interferogram, chosen by us through all of the frames of the movie. Once, we produce the spatial interferogram (signal vs. pixel) we use the interferometric formula (see Eq. 1) integrated as code in VBA macros in Microsoft Excel. The formula is as follows:

$$h = \frac{\lambda}{2\pi n_0} \left[ l\pi \pm \arcsin \sqrt{\frac{\Delta(1+r)^2}{(1-r)^2 + 4r\Delta}} \right] \quad (1)$$

where  $\lambda$  is the wavelength of the monochromatic light after digital filtration (for green light  $\lambda = 551$  nm),  $n_0$  is the refractive index of water ( $n_0 = 1.333$

at  $T=20^\circ\text{C}$ ),  $l$  is order of interference,  $\Delta=(I-I_{min})/(I_{max}-I_{min})$ , where  $I$  is the transient strength of the signal,  $I_{max}$  and  $I_{min}$  are its maximal and minimal values,  $r=(n_0-n_1)^2/(n_0+n_1)^2$  is the Fresnel reflection coefficient,  $n_1$  is the refractive index of the air ( $n_1=1$ ). The minimal signal for the foam film is usually taken from the signal of a ruptured film while the maximal signal is taken from the digital interferogram.

### *Study of pneumatic foams*

Dynamic foam analyzer (DFA – 100, Kruss ltd, Germany) was used to study the foams. The pneumatic foams were produced by means of sparging of gas (0.3 L/min) through the porous bottom of a column containing the foaming solution. After turning on the gas flux, the foam column starts raising up until reaching a certain maximal height at which the gas delivery is switched off, thus allowing the foam to decay. Both, the foam upraise and the foam decay are monitored by means of scanline camera which delivers the foams image to a computer whose specialized software digitalizes this image and records it. This allows us to record the height of the foam vs. time and calculate in this the rates of foam upraise and decay, its lifetime and the foam production number:

$$f = V_{foam\ min\ g} / V_{defoam\ min\ g} \quad (2)$$

The chemicals LiCl, NaCl and KCl were purchased from Sigma-Aldrich.

## RESULTS AND DISCUSSION

Foam films and foams stabilized by 0.05 mmol/L SDS in presence of LiCl, NaCl and KCl in the concentration range of 1.1 mmol/L to 50 mmol/L were explored.

### *Exploration of the ion-specific effects on foam films stabilized by 0.05 mmol/L SDS*

The equilibrium foam films for each one of the cases were obtained by means of the above-mentioned interferometric method. The surface potentials of the foam films in presence of each one of the salts were calculated by means of the DLVO theory [22]. The equilibrium foam film thickness and its correspondent surface potential values vs. the added salt concentration are presented in Fig. 1. One can see that both the equilibrium film thickness and the surface potential values in the cases of LiCl, NaCl and KCl practically coincide in their whole concentration range. This is an indication that no counter ion-specific effect in the particular case of 0.05 mmol/L SDS can be registered.

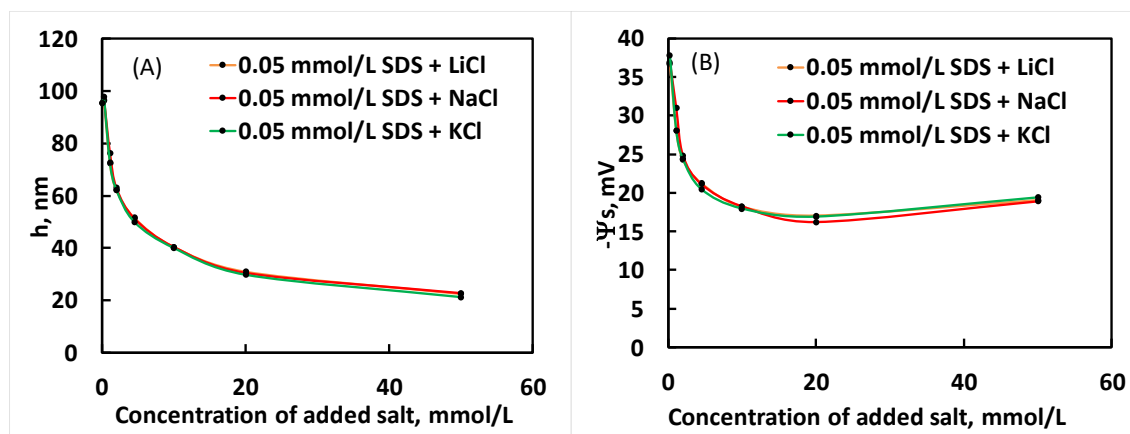


Figure 1. Equilibrium foam film thickness (A) and surface potential (B) of foam films stabilized by 0.05 mmol/L SDS vs. concentration of the added salt (LiCl, NaCl, KCl).

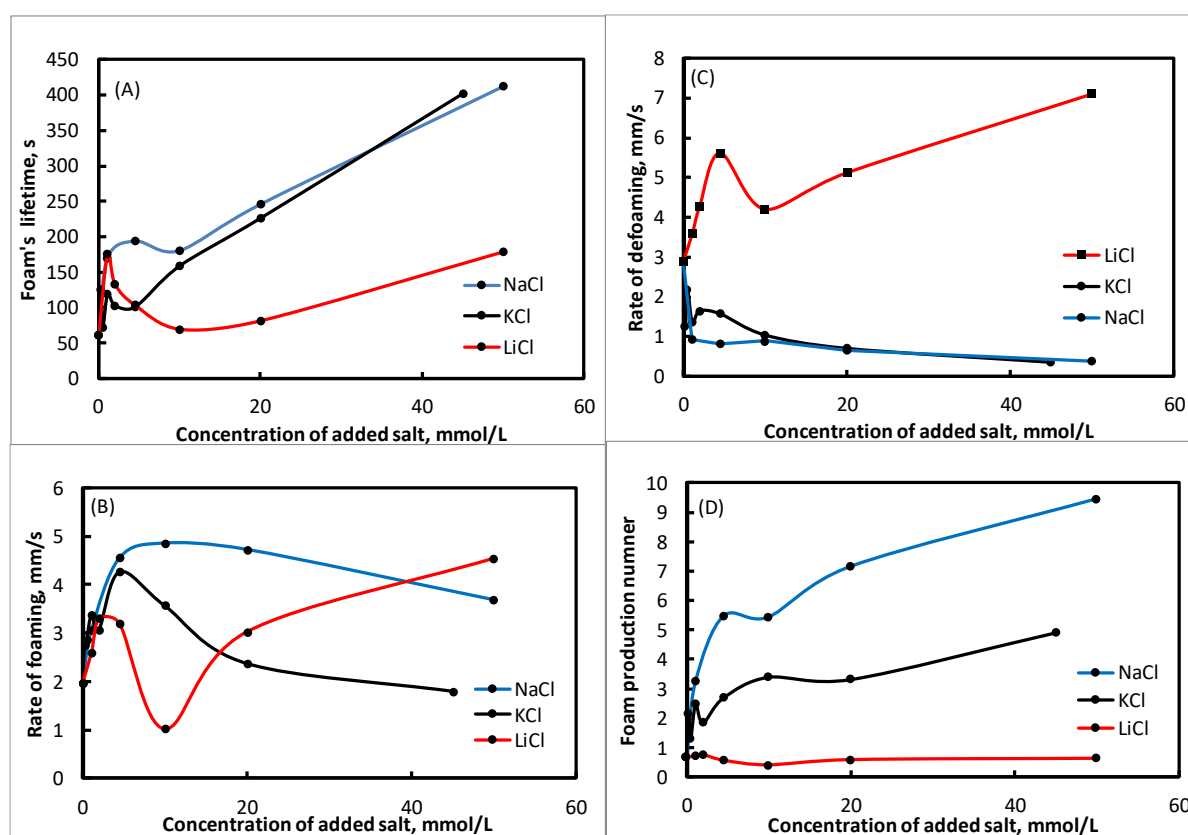


Figure 2. Foam's lifetime (A), rate of foaming (B), rate of defoaming (C) and foam production number (D) vs. the concentration of the added salt.

#### Exploration of the ion-specific effects on pneumatic foam stabilized by 0.05 mmol/L SDS

The foam's lifetime, the rate of foaming, the rate of foam decay and the foam production number versus the added salt concentration for the three different cases (0.05 mmol/L SDS + LiCl, NaCl, KCl) is presented in Fig. 2. The salt – specific effect on the foam films stabilized by 0.05 mmol/L SDS was not observed, but it was registered in the case of the pneumatic foams produced from the same SDS + MCl ( $M = \text{Li, Na, K}$ ) aqueous solutions. Obviously, the ion-specific effect for this very

diluted solution of SDS (0.05 mmol/L) emerges under dynamic conditions, while it vanishes under static conditions. In short, both NaCl and KCl significantly increase the foam's lifetime, while LiCl moderately increases the latter (see Fig. 2A). The rate of foaming reaches a maximum at certain concentrations of NaCl and KCl, above which it diminishes, while in the case of LiCl a peculiar and opposite trend is observed (see Fig. 2B). The rate of foam decay weakly diminishes upon the increase of the concentrations of NaCl and KCl, while it raises steeply in the case of LiCl (see Fig. 2C). One can see

most clearly the effect of the type of salt on the foam's behavior in Fig. 2D. The foam production number steeply increases with the increase of the concentration of NaCl, followed by KCl, in which it increases weaker than in the case of NaCl. In the case of LiCl the foam production number practically does not depend on the concentration of LiCl, but it is below unity, which means that LiCl acts as a weak foam suppressor. On the contrary, KCl and NaCl act like foam boosters with NaCl being the strongest one.

### CONCLUSIONS

The counter-ion-specific effect on a very diluted solution of SDS (0.05 mmol/L) was studied by means of added LiCl, NaCl and KCl. No effect of the type of the salt on the equilibrium foam films was established, while in the case of pneumatic foams NaCl acted as a strong foam booster, followed by KCl. The third salt (LiCl) showed a peculiar effect on the foam but generally it acted as a weak foam suppressor not depending on the LiCl concentration.

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