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Counter-Ion Effect on the Surface Potential of Foam Films and Foams Stabilized by 0.5 mmol/L Sodium Dodecyl Sulfate

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Abstract: It is well known that the type of counter-ion affects the state of the adsorption layer of ionic surfactants and, consequently, its surface potential. Yet, it is not clear how they affect the foamability, the rate of foam decay or foam production. How is the surface potential of the air/water interface related to the properties of the foam? This work aims to answer these questions. Foam films, stabilized by 0.5 mmol/L sodium dodecyl sulfate (SDS) in the presence of added LiCl, NaCl, and KCl, were studied by means of the interferometric experimental setup of Scheludko–Exerowa. The surface potential values were derived from the equilibrium film thickness by means of the DLVO theory. A linear relation between the values of the surface potential and specific adsorption energy of the counter-ions on the air/water interface was established. The slope of this linear relation depends on the salt concentration. The foamability, the rate of foam decay, and the foam production of the same aqueous solutions of SDS and added salts were studied by means of the shaking method. A correlation was found between the derived surface potential of the foam film's surfaces and the properties of the foam. The foam production, which is the ratio between the initial foam volume and the rate of foam decay, increases with the decrease in the surface potential. Previous studies in the literature confirm that the lower surface potential promotes higher surfactant adsorption, thus boosting more foam and vice versa. It was also confirmed that the dual effect of KCl on foam production involves converting the best foam stabilizer into a foam suppressor at the highest salt concentration.

Keywords: ion-specific effects; foam films; foam; DLVO

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1. Introduction

The ion-specific effects were first discovered by Professor Hofmeister and his coworkers at the end of XIX century [1–6]. They established that some inorganic salts are stronger precipitators of blood proteins than other salts. They proved that both cations and anions of salts have an additive contribution to the precipitation of the blood proteins. Thus, they ordered them in a series of increasing precipitation abilities:

$$Li^+ < Na^+ < NH_4^+ < K^+ < Cs^+ < OH^- < F^- < CH_3COO^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- \quad (1)$$

The ion order in this series was found to be independent of the nature of the proteins, although the effect depends on the net charge of the proteins. Moreover, they established that the salts precipitate identically isinglass, colloidal ferric oxide and sodium oleate, thus showing the broad scope of the ion-specific effects. These pioneering studies set the beginning of a new field in the colloidal sciences. Since that time, a significant effort has been made to unveil the nature of the ion-specific effects. The scope of these effects appeared to be significantly broader. For example, Heydweiller established [7] that the inorganic salts increase the surface tension of their aqueous solutions. Weissenborn and Pugh [8,9] found that the increment of the surface tension is a result of the additive contribution of the cations and anions following the Hofmeister series. Similarly, they reported that the salts inhibit the bubble coalescence at certain transition concentrations, being either stronger or weaker coalescence inhibitors, following the Hofmeister series. The Jones–Dole viscosity coefficients of the salt solutions are affected identically. They made a correlation with the entropy of hydration of the cations and anions, but this did not help much. An excellent review of Marcus [10] shows a good correlation between the increment of the surface tension and surface potential values and the sizes, polarizabilities, and hydration shells of the ions. Yet, correlations are helpful, but they are not theories. Thus, Ninham was the first [11] to account for the van der Waals interactions between the ions and the hydrophobic surfaces despite being air/water interface, proteins or colloidal particles [12–14]. Their efforts met difficulties [15–17]. Molecular dynamic simulations conducted by Jungwirth and coworkers [18,19] reported that the larger the polarizability of the ions, the larger their propensity to adsorb on the air/water interface and vice versa.

Another team of Polish scientists headed by Warszynski studied the counter-ion effects on the adsorption layers of ionic surfactants [20–22]. They conducted thermodynamic analysis, thus confirming the correlation between the polarizability of the ions and their surface activity regarding the air/water interface. Moreover, the size of ions appeared to be crucial due to their hydration, thus dividing the ions into chaotropes and kosmotrops, affecting not only their adsorption on the air/water interface but the stability of dispersions, amphiphilic molecules, and the formation of ion pairs [23–26].

A Bulgarian team headed by Ivanov and coworkers [27] followed Ninham's approach, proposing and validating a relatively simple theory about the effect of the type of added electrolyte on the adsorption constant of the ionic surfactants. The ion specificity is expressed by the ion-specific adsorption energy u_0/k_BT (k_B is the Boltzmann constant, T is absolute value of the temperature), which is equal to the dispersion energy of adsorption of the ions on the air/water interface and operates with the basic parameters of the ions and water molecules—polarizability, the ionization potential, the radius of the hydrated ion and the possible deformation of the hydration shell upon the ion adsorption at the air/water interface. It is independent of the presence of surfactant, which allows one to combine theoretically the contributions from every type of counter-ion with all the possible surface active co-ions. Ref. [28] applied this theory to the disjoining pressure of thin liquid films and emulsion stability. According to this theory, the counter-ions with smaller absolute values of the specific adsorption energy penetrate less in the surfactant adsorption layer, thus rendering a higher value of the surface potential, resulting in stronger electrostatic repulsion between the film surfaces. This should electrostatically stabilize the foam or the emulsion. Surprisingly, the opposite trend was observed. Emulsions having such type of counter-ions were the least stable and vice versa. This was explained by the larger electrostatic barrier of the adsorption of the surface-active co-ions. Experimental verification of the stability of foam stabilized by sodium dodecyl sulfate in the presence of LiCl, NaCl and KCl was conducted in ref. [29]. The observations from ref. [28] for emulsion stability were confirmed for foam stability. Refs. [30,31] studied the effect of the added co-ions and counter-ions on thin foam films containing sodium dodecyl sulfate by means of the thin film pressure balance method and made a correlation between the surface potential and the size of the co-ions and counter-ions. Surprisingly, they overlooked the theory of Ivanov et al. [27] about the specific energy of counter-ion adsorption on the air/water interface. Meanwhile, an intensive effort has been put into studying the effect of counter-ions on the foam [22,32–35] under different conditions. In all cases, the stability of the foam decreases with the size of the counter-ions. There is no work relating the properties of the foam films, the specific energy of the counter-ion adsorption on the air/water interface with foamability and the rate of foam decay.

This work aims to fill the missing gap in the literature relating the specific energy of counter-ion adsorption governing the surface potential of the foam film, foamability and the rate of foam decay. Foam films stabilized by 0.5 mmol/L sodium dodecyl sulfate in the presence of added electrolytes (LiCl, NaCl and KCl) in the concentration range of 5.5 mmol/L to 40 mmol/L were studied. This experiment allowed us to determine the equilibrium film thickness interferometrically for each one of the studied cases. Hence, we used the DLVO theory [36–38] to calculate the values of the surface potential of the foam films. Hence, we made a correlation between these values and the values of the specific energy of counter-ions adsorption on the air/water interface.

This allowed us to determine the counter-ion effect on the foamability and the foam durability separately. In addition, it relates the counter-ion effects with the surface production, unifying the foamability and foam durability.

2. Materials and Methods

2.1. Materials

Experiments on foam films stabilized by 0.5 mmol/L SDS and in the presence of LiCl, NaCl and KCl in the concentration range of 5.5 mmol/L to 40 mmol/L were conducted.

All the chemicals (SDS, LiCl, NaCl, and KCl) were purchased from Sigma-Aldrich (Darmstadt, Germany) and SDS was purified by means of three times recrystallization with ethanol. The salts were heated at T = 800 °C for 3 h to burn out any inorganic contaminants. The deionized water was produced by Millipore water purification system.

2.2. Methods

2.2.1. Interferometric Study of Foam Films

The interferometric method for studying thin liquid films allows one to calculate the surface potential of the film surface [39]. 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 a 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-concaved drop. After this, the two tips of the double-concaved drop are approached toward each other by means of 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 (λ = 551 nm) generated by an inverted microscope (Carl Zeiss, Jena, Germany) and reflected by the two surfaces of the film, causing the appearance of two phase-shifted beams of reflected light, which are collected together and captured by a Sony—SSC-M388CE photocamera as a temporal general interferogram. The latter is recorded on a computer as a movie in "avi" format. "Image J" software, version 1.53a. is used for processing the movie. Hence, the movie of the evolution of the general interferogram is split into pictures in 0.083 s per 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 Equation (1)) integrated as code in VBA macros in Microsoft Excel of Microsoft Office Professional plus 2016 The formula is the following:

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

where λ 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 °C), l is the order of interference, $\Delta = (I - I_{\min})/(I_{\max} - I_{\min})$, 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, and 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.

2.2.2. Surface Tension and Capillary Pressure

The surface tension of each one of the solutions was measured by means of the Wilhelmi plate method 15 min after positioning the solution into the experimental cell. The average measurement error was estimated to be 0.5 mN/m. The measurement of the surface tension allowed us to calculate the capillary pressure P_σ, which is the drainage driving force of the foam films in the interferometric experiment:

$$P_c = \frac{2\sigma}{R}, \tag{3}$$

where σ is the surface tension and R is the radius of the film holder. The action of the capillary pressure does not depend on the film thickness, while the electrostatic disjoining pressure, emerging due to the electrostatic repulsion between the film surfaces, enhances its value upon the decrease in the film thickness until achieving equality between the two pressures, at which the films do not drain anymore and come into equilibrium. There is a second disjoining pressure, the van der Waals, emerging from the cohesion of the water molecules into the aqueous core of the film thickness. This pressure for the particular case of the foam films is attractive, but it is short ranged and becomes significant below 30 nm. Both pressures are unified and described by the celebrated DLVO theory [36–38].

2.2.3. Foam

The experiments on the foam are described in ref. [40]. In short, 50 mL from the foaming solution was situated in 250 mL column of Bartsch. The foam was produced by means of 10-fold energetical shaking. The initial foam volume and the kinetics of foam decay were monitored and recorded by a camera and processed offline.

2.2.4. Methodical Processing of the Results

The equilibrium thickness of foam films stabilized by 0.5 mmol/L SDS was determined at different concentrations of added salt (LiCl, NaCl, KCl) in the concentration range of 5.5 mmol/L to 40 mmol/L. It is evident that the counter-ions, introduced by the added salt, are in great excess compared to the intrinsic counter-ions of SDS (Na^+ ion). Once the equilibrium film thickness was determined, the surface potential of the foam films for each particular case was calculated using the DLVO theory [36–38]. The total electrolyte concentration was converted into activity for each particular salt and case using the theory of Pitzer [41,42]. The mean ion activity of the mixture (surfactant + salt), the equilibrium film thickness and the capillary pressure were used as input parameters to the DLVO theory to calculate the surface potential values of the foam films for each particular case.

The electrostatic disjoining pressure Π_{el} was calculated by the following equation, assuming constant surface potential; it is valid until the value of the surface potential reaches $\varphi_s \approx 120$ mV [43]:

$$\Pi_{el}(h) = 32 c_{el} R_g T \tanh^2\left(\frac{y_0}{4}\right)\left\{\frac{1}{1+\cosh\kappa h} + f(y_0)\sinh^2\frac{y_0}{4}\exp[-f(y_0)kh]\right\} \tag{4}$$

where c_{el} is the molar concentration (in SI units) of electrolytes in the solution. It is usually equal to the concentration of the ionic surfactant in the absence of added salt or to the background electrolyte concentration due to the dissolved carbon dioxide from the air ($\approx 5 \times 10^{-3}$ mmol/L) in the presence of the non-ionic surfactant. For the case of the ionic surfactant in the presence of added salt in significant excess c_{el} is the mean ion activity $c_{el} = \sqrt{a_s(a_s + a_{salt})}$, where the Debye constant for a binary electrolyte of valence z is defined as $\kappa = \left\{2c_{el}F^2z^2/\left(\varepsilon\varepsilon_0 R_g T\right)\right\}^{1/2}$, where ε_0 is the dielectric permittivity of the vacuum. The normalized surface potential is defined as $y_0 = zF\varphi_s/\left(R_g T\right)$, where F is the

Faraday constant and ψ_s is the surface potential. For $|y_0| \leq 7$, the function $f(y_0)$ is defined as $f(y_0) = 2\cosh(0.332|y_0| - 0.779)$.

The van der Waals disjoining pressure, Π_{vdW}, as a function of the film thickness, h, for both the nonretarded and retarded regimes can be described as [38]

$$\Pi_{vdW} = -\frac{A(h,\kappa)}{6\pi h^3} + \frac{1}{12\pi h^2}\frac{dA(h,\kappa)}{dh} \tag{5}$$

where $A(h,\kappa)$ is the Hamaker–Lifshitz function, which depends on the film thickness and the Debye constant, κ, due to the electromagnetic retardation effect and is described as

$$A(h,\kappa) = (1+2\kappa h)e^{-2\kappa h}\frac{3k_BT}{4}\sum_{j=1}^{\infty} j^{-3}\left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{2j} + \frac{3\hbar\omega}{16\sqrt{2}}\frac{\left(n_1^2-n_2^2\right)^2}{\left(n_1^2+n_2^2\right)^{3/2}}\left\{1+\left(\frac{h}{\widetilde{\lambda}}\right)^q\right\}^{-1/q} \tag{6}$$

where ε_1 is the static dielectric permittivity of the dispersion phase (2.379 for toluene at 298.15 K), ε_2 is the static dielectric permittivity of the dispersing medium (80 for water), $\hbar = 1.055 \times 10^{-34}$ Js/rad is the Planck constant (divided by 2π), ω is the absorption frequency in the UV region, typically around 2.068×10^{16} rad/s for water, and n_1 and n_2 are the characteristic refractive indices of the dispersion phase and the medium of $n_1^2 = 1$ for air and $n_2^2 = 1.887$ for water, and $q = 1.185$. The characteristic wavelength is defined as $\widetilde{\lambda} = 2v\sqrt{2/n_2^2\left(n_1^2+n_2^2\right)}/\left(\pi^2\omega\right)$, where v is the speed of light.

3. Results

3.1. Counter-Ion Specific Effects on Thin Foam Films Stabilized by 0.5 mmol/L SDS

Figure 1 shows the surface tension values of 0.5 mmol/L SDS as a function of the concentration of added salts—LiCl, NaCl, and KCl.

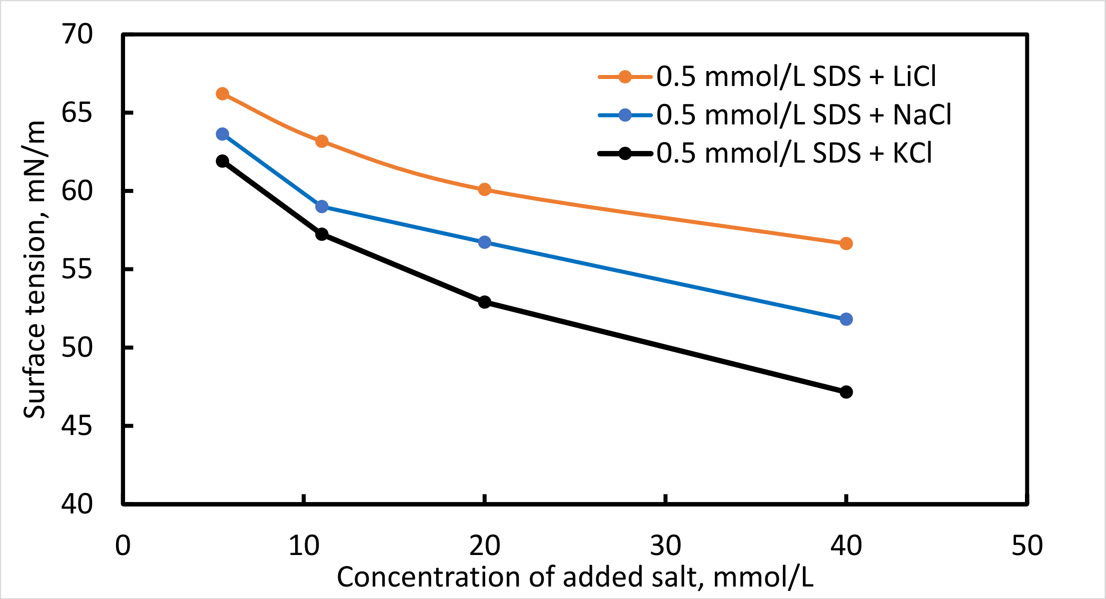


Figure 1. Surface tension values of 0.5 mmol/L SDS versus the concentration of the added LiCl, NaCl, KCl.

The effect of the type of counter-ion on the surface tension of the aqueous solution of SDS is evident in Figure 1. One can see that the surface tension decreases with the increase in the salt concentration, but the decrement of this decrease depends on the type of counter-ion. The strongest decrease in the surface tension happens with K$^+$ counter-ions, followed by Na$^+$ and Li$^+$ counter-ions. Now, the point is how the type of the counter-ion affects the equilibrium thickness of the foam films at a fixed concentration of SDS.

One can see in Figure 2 the equilibrium thickness of the foam films, stabilized by 0.5 mmol/L SDS versus the concentration of the added salt (LiCl, NaCl, and KCl). The equilibrium film thickness decreases with increasing the concentration of the added salt. Yet, again, the decrement of this dependence is affected by the type of counter-ion. The strongest effect is the K^+ counter-ion, followed by Na^+ and Li^+ counter-ions.

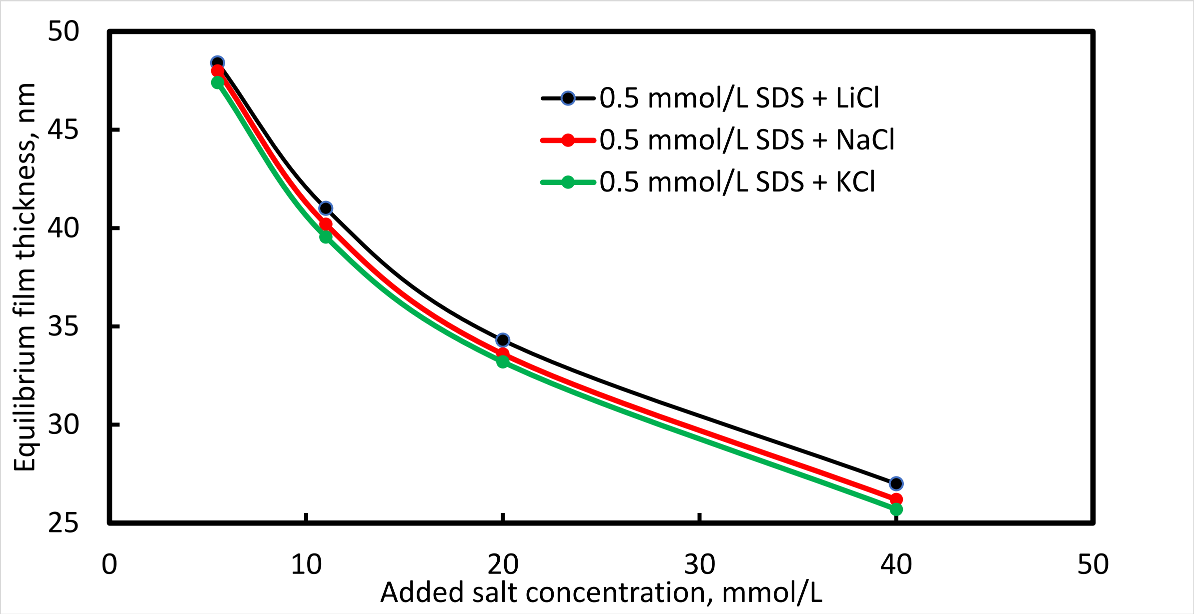


Figure 2. Equilibrium thickness of foam films stabilized by 0.5 mmol/L SDS versus the concentration of the added LiCl, NaCl, and KCl.

The DLVO theory was applied, as described here above, to calculate the surface potential of the foam films.

Figure 3 shows the surface potential values of the foam films versus the concentration of the added LiCl, NaCl, and KCl. The surface potential value decreases with the increase in the concentration of the added salt. Here again, the K^+ counter-ion causes the strongest decrease in the surface potential, followed by the Na^+ and Li^+ counter-ions. This difference can be explained by the different propensity of the counter-ions to adsorb on the air/water interface, decreasing the value of the surface potential in a medium of surface active co-ions adsorbed on the air/water interface. The propensity of the ions to adsorb on the air/water interface can be described with their specific energy of adsorption on the interface [44,45]. This energy can be calculated using the basic parameters of the ions—their radii, polarizability and ionization energy (for details, see refs. [44,45]). The larger the specific energy of adsorption on the air/water interface, the larger the adsorption of the ion. Hence, the counter-ions with a larger specific energy of adsorption decrease the surface potential to a greater degree than the counter-ions with less specific energy of adsorption.

Figure 4 shows the dimensionless surface potential of the foam films at different concentrations of added electrolyte versus the specific energy of adsorption of the counter-ions in the present study. One can see that the surface potential decreases linearly with the increase in the absolute value of the specific energy of adsorption. The slope of this linearity decreases with the increase in the salt concentration. Moreover, we can calculate from the intercepts in Figure 4 the surface potential of the foam films if the counter-ions do not adsorb on the air/water interface at all ($-u_0/k_BT = 0$). They are presented in Figure 3 (the red line signified pure surface potential). One can see in Figure 3 that the surface potential in the presence of LiCl practically coincides with the pure surface potential, which is an indication of the negligible adsorption of the Li^+ counter-ions on the air/water interface.

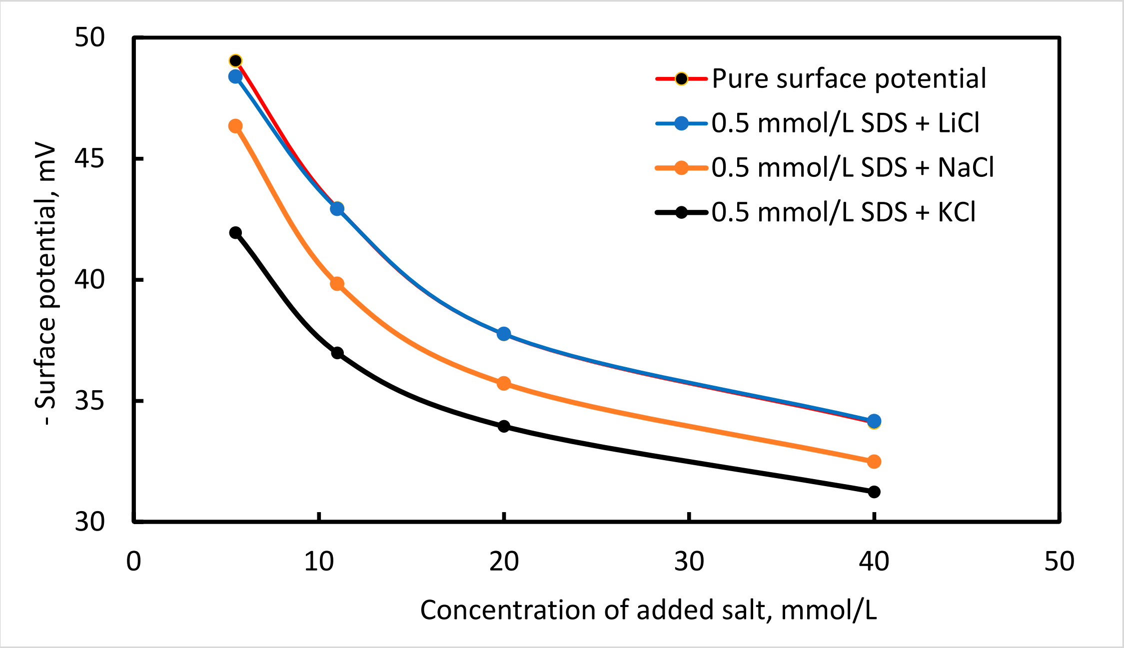


Figure 3. Surface potential of foam films stabilized by 0.5 mmol/L SDS versus the concentration of the added LiCl, NaCl, KCl; the red line represents the surface potential versus the concentration of added salt but with excluded adsorption of the counter-ions.

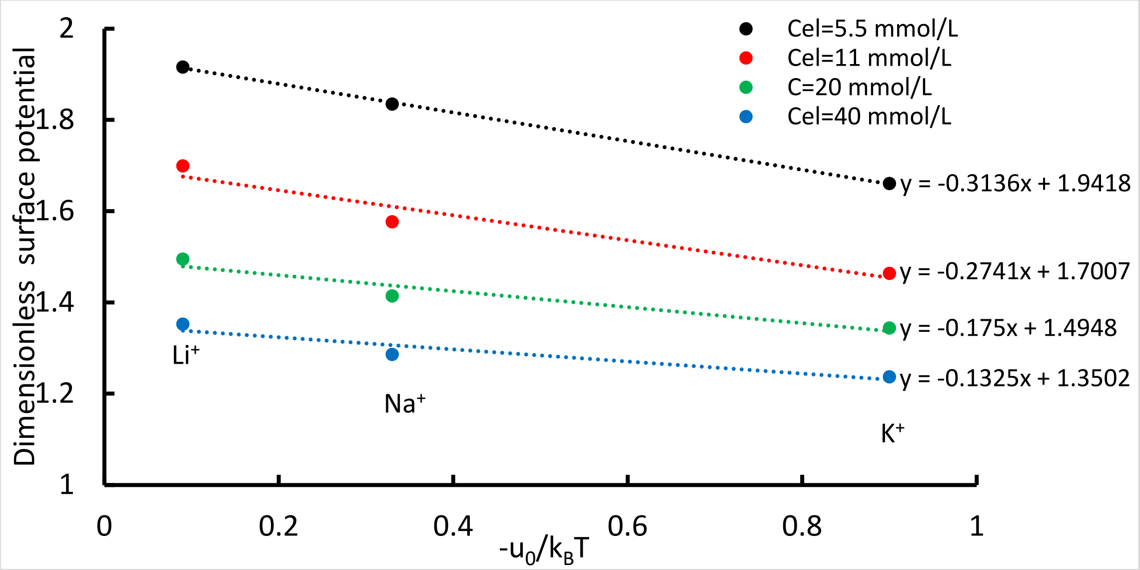


Figure 4. Dimensionless surface potential $F\varphi_s/R_gT$ of the foam films at different concentrations of added salts versus the specific energy of adsorption $-u_0/k_BT$ of Li^+, Na^+ and K^+ counter-ions.

As far as we calculated the surface potential for each particular case, we calculated its corresponding DLVO curves in terms of the disjoining pressure of the foam films versus the thickness of the foam films.

Figure 5 shows the disjoining pressure—film thickness DLVO curves for each particular concentration of the added salt. It is evident that the potential barrier decreases with the increase in the concentration of the added salt. Moreover, the counter-ions with larger absolute values of the specific adsorption energy contribute to the small potential barrier of the DLVO curve and vice versa. This is in line with the theoretical expectations. In addition, one can see that the DLVO curve with Li^+ counter-ions almost coincides with the theoretical one corresponding to a zero value of the specific adsorption energy of the counter-ions. As long as the counter-ion effect on the properties of the foam films in the present study is in line with the theoretical expectations, it is questionable how the counter-ions could affect the foamability, the rate of the foam decay and the foam production of the same particular aqueous solutions of 0.5 mmol/L SDS + added salts.

3.2. Counter-Ion Specific Effects on Foam, Stabilized by 0.5 mmol/L SDS

We will begin with correlations between the initial foam volume and the specific energy of adsorption of the counter-ions of the added salt on the air/water interface for each of the concentrations of the added salt.

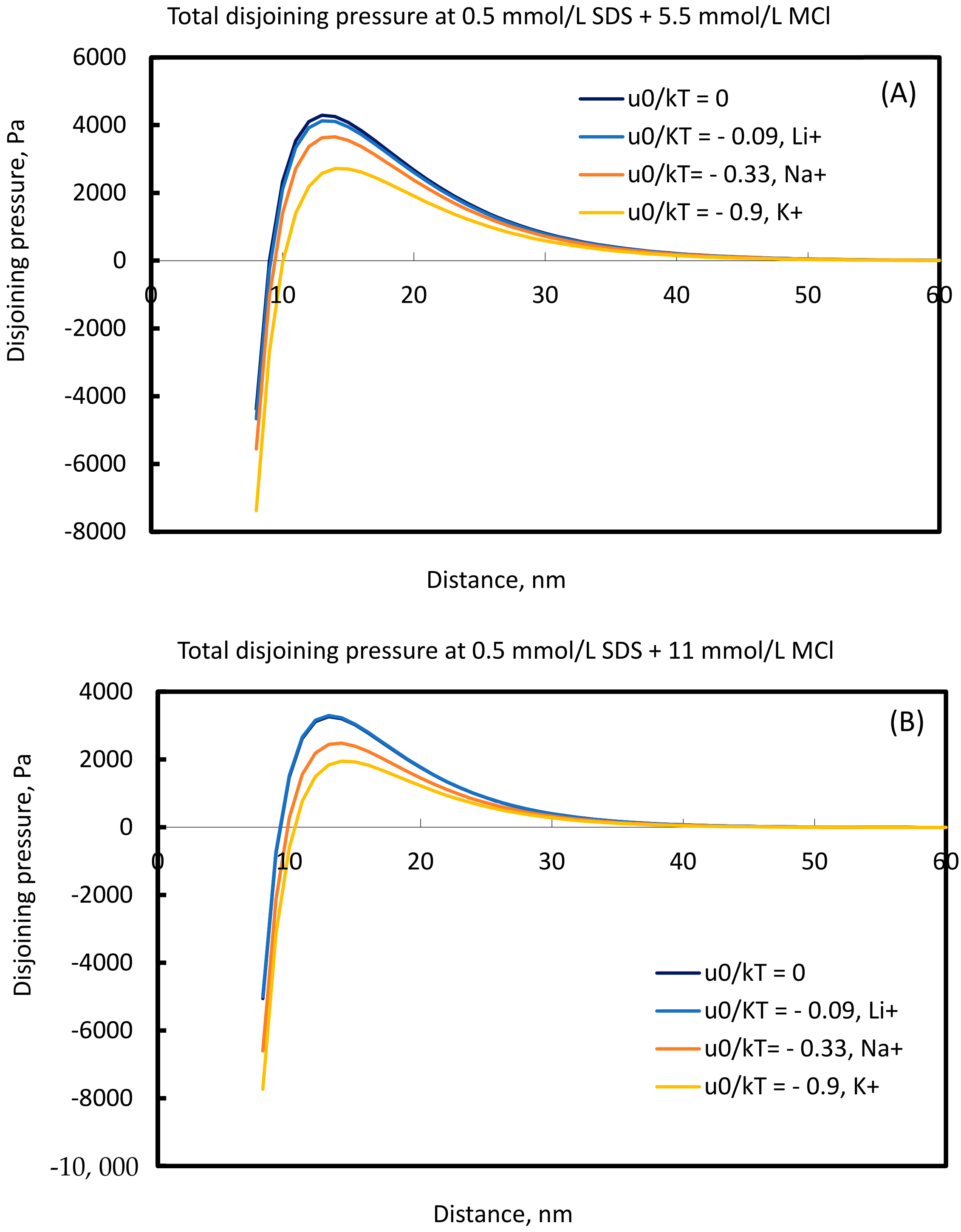


Figure 5. *Cont.*

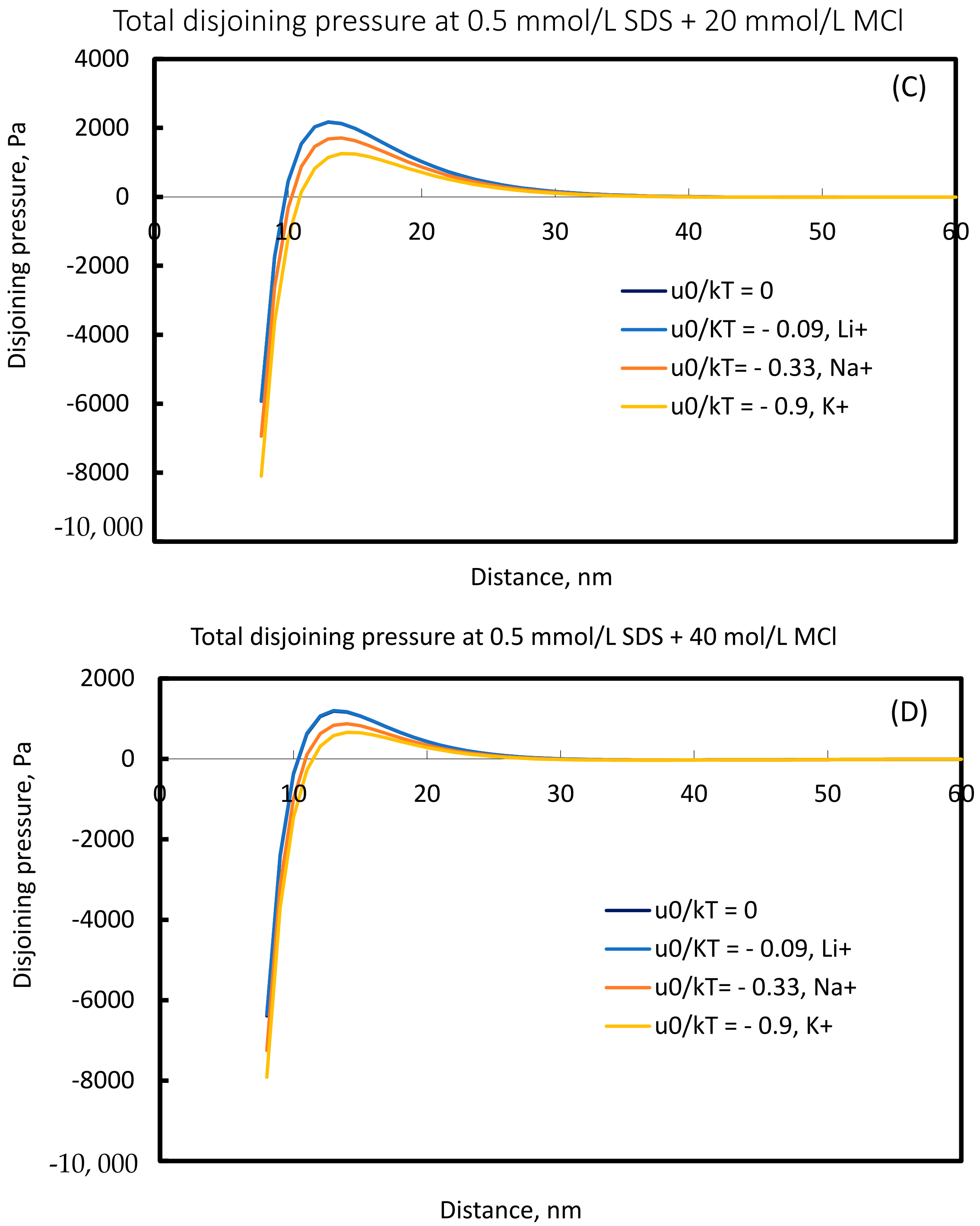
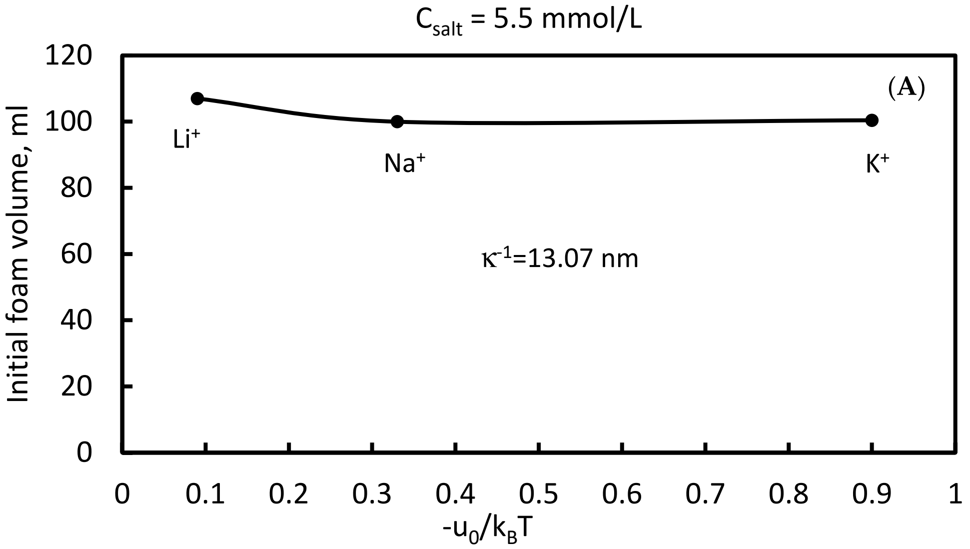


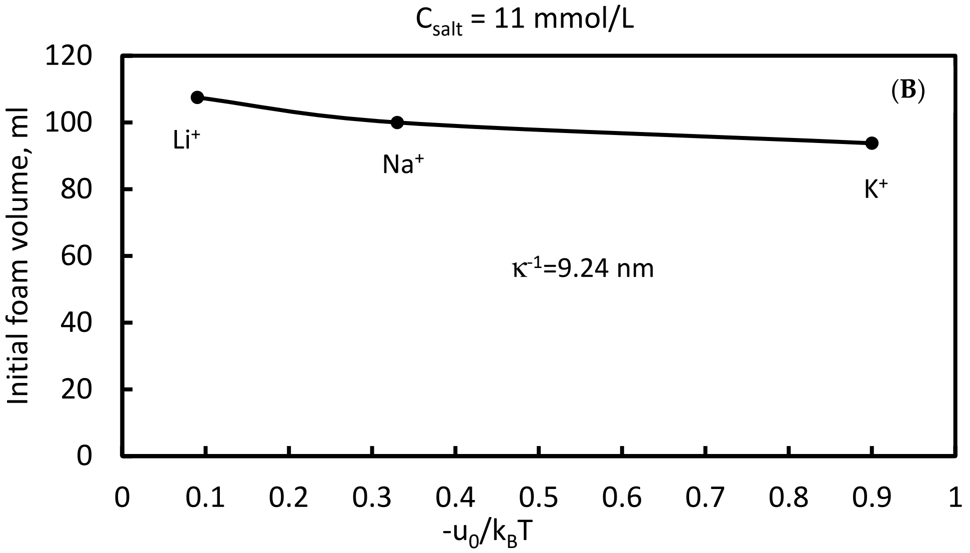
Figure 5. Total disjoining pressure versus distance between the film's surfaces for the cases of (**A**) 5.5 mmol/L added salt; (**B**) 11 mmol/L added salt; (**C**) 20 mmol/L added salt; (**D**) 40 mmol/L added salt.

The initial foam volume for each particular concentration of added salt versus the specific absorption energy of the counter-ions on the air/water interface is presented in Figure 6. One can see that the initial foam volume practically does not depend on the specific energy of adsorption of the counter-ions for the first two concentrations of the added salt, 5.5 mmol/L and 11 mmol/L, while it decreases with the increase in the absolute value of $-u_0/k_BT$ at 20 mmol/L and 40 mmol/L. If one looks more precisely at the graphs in Figure 6, it is observed that the Na^+ counter-ions have hardly any effect on the foamability despite the concentration of the added NaCl. Li^+ counter-ions increase the foamability slightly with the increase in the concentration of LCl, while K^+ counter-ions decrease the foamability with the increase in the concentration of KCl.

It is interesting to study the effect of the type of the counter-ions on the rate of foam decay of the same systems.

Figure 7 shows the initial rate of foam decay versus the specific energy of adsorption of the counter-ions for each particular concentration of the added salt. One can see that the rate of foam decay decreases with the increase in the absolute value of the specific energy of adsorption and the dependence becomes stronger by increasing the concentration of the added salt. In the case of KCl, the K^+ counter-ions cause reaching a minimum in the rate of the foam decay at 20 mmol/L and 40 mmol/L added salt. In the case of NaCl, Na^+ counter-ions cause a decrease in its rate of foam decay by increasing its concentration in the whole concentration range of 5.5 mmol/L to 40 mmol/L. In the case of LiCl, the Li^+ counter-ions have practically no effect on the rate of foam decay at any of the concentrations of the added LiCl.





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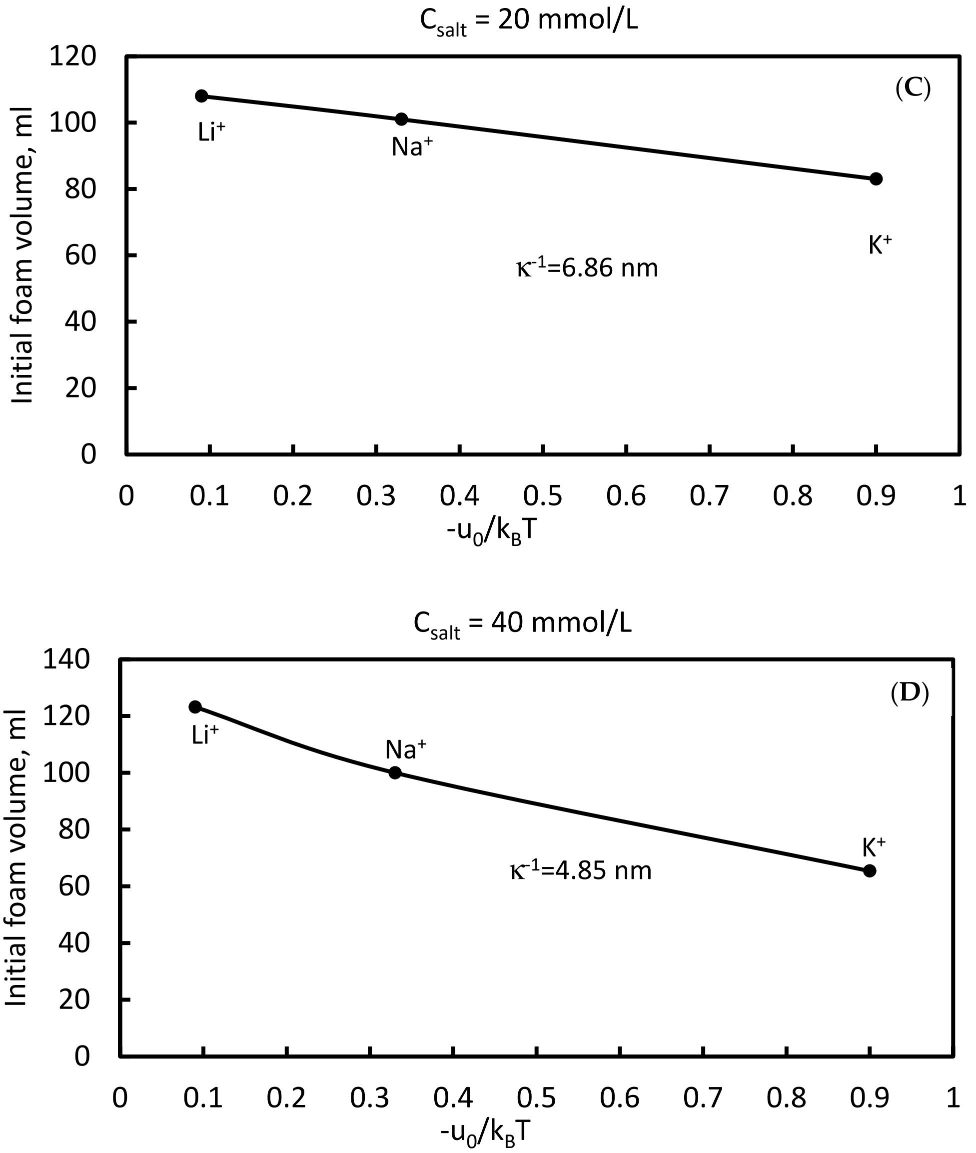
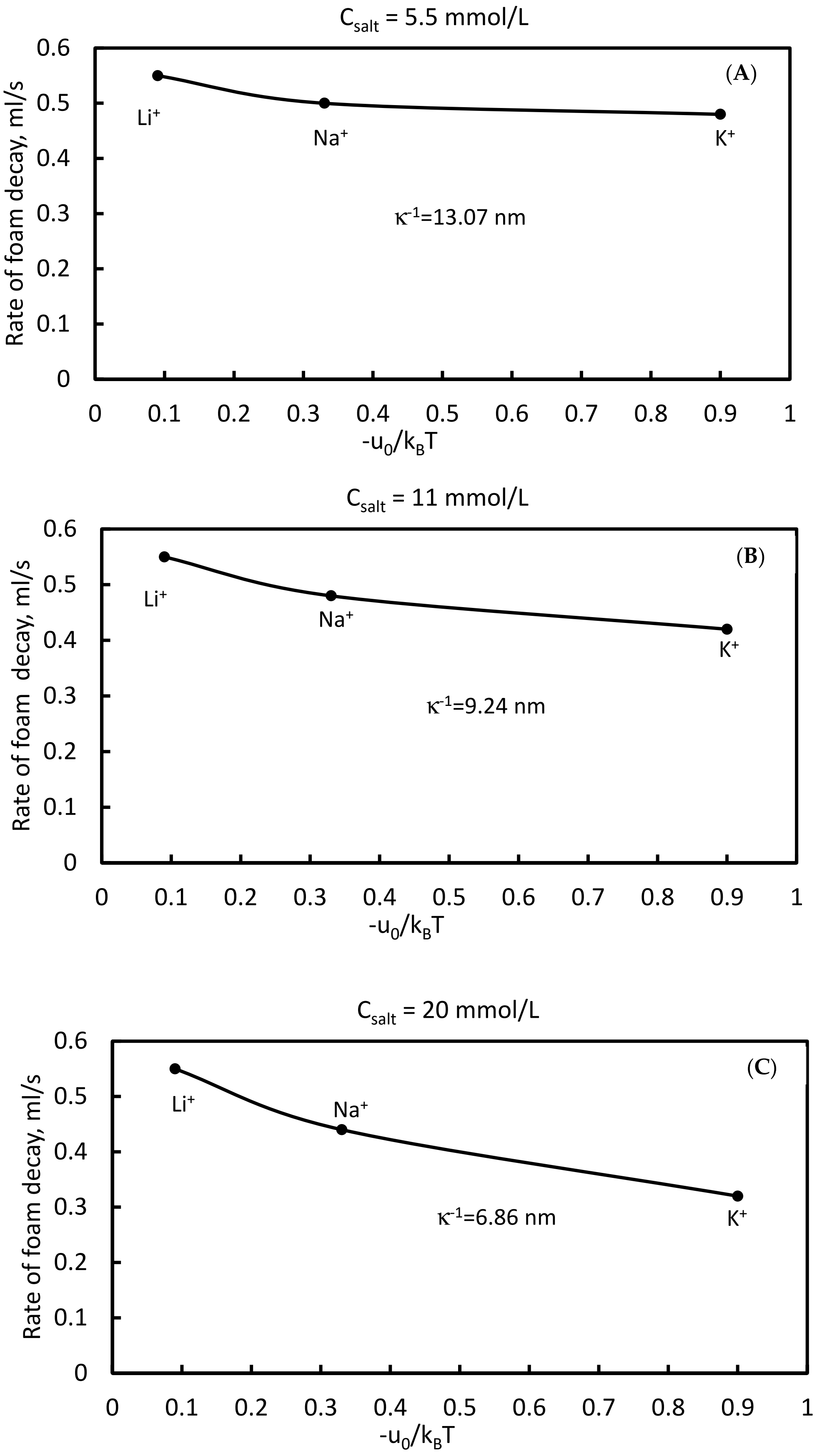


Figure 6. Initial foam volume versus the specific adsorption energy of the counter-ions on the air/water interface for (**A**) 5.5 mmol/L added salt; (**B**) 11 mmol/L added salt; (**C**) 20 mmol/L added salt; (**D**) 40 mmol/L added salt. The inverted Debye length for each particular case is presented as well.

If one unifies the experimental data from Figures 6 and 7, it could be concluded that Li^+ counter-ions slightly increase the foamability of the system but do not affect the rate of foam decay. Keeping in mind that Li^+ counter-ions almost do not adsorb on the air/water interface, one could conclude that this effect is non-ion-specific, contributing only to its screening effect on the electrostatic field in close proximity to the bubbles. With NaCl, Na^+ counter-ions do not affect the foamability at any concentration, but decrease the rate of foam decay with the increase in the concentration of NaCl. With KCl, K^+ counter-ions decrease both the foamability and the rate of foam decay with increasing the concentration of KCl. These three different effects on the foamability and foam durability might be difficult to understand. For this reason, we applied our concept for foam production—the ratio between the initial foam volume and initial rate of foam decay.



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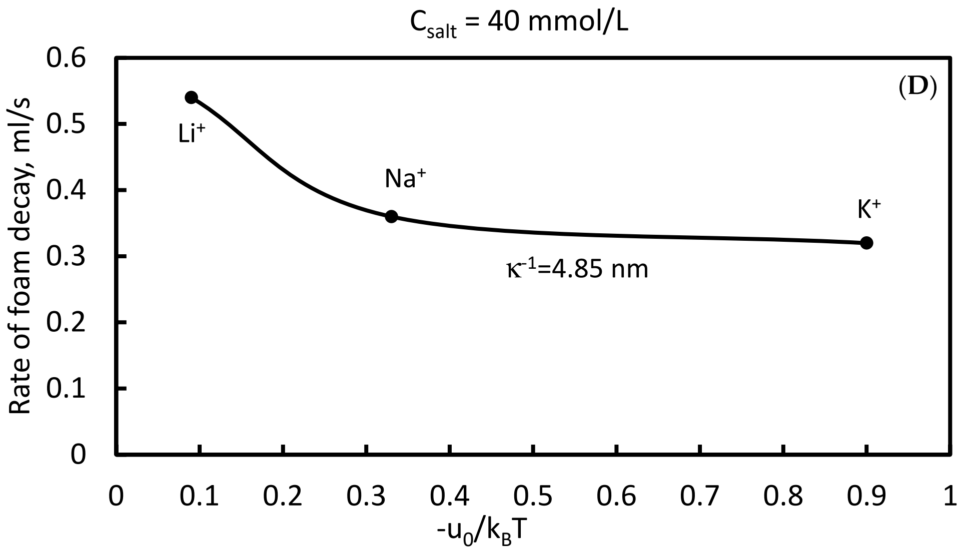

Figure 7. Initial rate of foam decay versus the specific adsorption energy of the counter-ions on the air/water interface for (**A**) 5.5 mmol/L added salt; (**B**) 11 mmol/L added salt; (**C**) 20 mmol/L added salt; (**D**) 40 mmol/L added salt. The inverted Debye length for each particular case is presented as well.

Figure 8 presents the foam production versus the absolute value of the specific energy of adsorption at different concentrations of the added salt. One can see that the foam production increases with the increase in the absolute value of the specific energy of adsorption. The slope of this dependence increases with increasing the concentration of the added salt in the range of 5.5 mmol/L to 20 mmol/L. This could be explained by the decrease in the surface potential of the bubbles, which should boost the adsorption of the dodecyl sulfate co-ions. It is interesting to note that the effect is purely ion-specific, as far as the increase in the concentration of LiCl in the same concentration range does not affect the foam production. Surprisingly, at 40 mmol/L added salt, the foam production jumps in the case of LiCl and NaCl, while it is significantly decreased in the case of KCl. The latter means that LiCl and NaCl suddenly become foam boosters, while KCl becomes a foam suppressor.

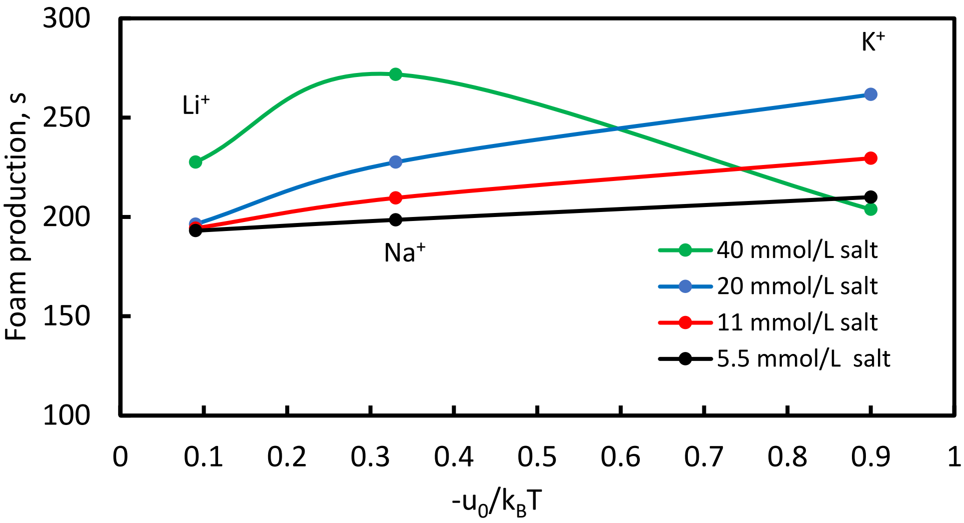

Figure 8. Foam production versus the specific adsorption energy of the counter-ions on the air/water interface for each one of the concentrations of added salt.

As seen in the former subsection, the counter-ions affect the surface potential of the foam films. Hence, the counter-ion-specific effects are expressed in affecting the surface potential of the bubbles. The value of the surface potential is responsible for the following: (i) the electrostatic repulsion between the bubbles; and (ii) the level of adsorption of the surface-active co-ions. Hence, it is appropriate to see the dependence of the initial foam volume, the initial rate of foam decay and the foam production on the surface potential value, as calculated in the former subsection. We should note that the surface potential values, calculated in the former subsection, belong to equilibrated foam films, while the generation of foam and the subsequent foam decay are dynamic processes. Nevertheless, correlations with these values can be developed.

Figure 9 presents the initial foam volume versus the surface potential volume of the equilibrated foam films, calculated in the former subsection, for all the concentration ranges of the added salt. One can see that the initial foam volume increases with the increase in the absolute value of the surface potential, especially for the concentration range of 11 mmol/L to 40 mmol/L. This is an indication of a certain level of electrostatic stabilization during the generation of the foam due to the electrostatic repulsion between the bubbles. In the case of 5.5 mmol/L of added salt, this dependence is not so strong. This is strange at first glance because a lower salt concentration corresponds to a reduced level of electrostatic screening. Although Figure 9 shows the clear dependence between the foamability and the electrostatic repulsion between the bubbles, it is still not illustrative.

Figure 10 is a group figure illustrating all the information presented by the more complex Figure 9. One can see in Figure 10 that, within the same concentration of the added salt, the increase in the absolute value of the surface potential causes larger foamability. In addition, one can follow the effect of certain counter-ions across the whole concentration range. For example, one can see that the increase in the concentration of KCl causes both a decrease in the absolute value of the surface potential of the foam films and a decrease in the foamability as well, and vice versa. This shows that the electrostatic stabilization controls the foamability during the production of the foam in the case of KCl. Interestingly, this is not the case for NaCl. The increase in the concentration of NaCl decreases the absolute values of the surface potential of the equilibrium foam films but it does not affect the foamability. The same is valid for the effect of LiCl, whose Li^+ counter-ions almost do not adsorb on the bubbles, but at 40 mmol/L cause an increase in foamability. We must recognize that during the generation of foam by the shaking method, the system is very far from equilibrium. The K^+ counter-ion, which has the highest absolute value of the specific adsorption energy, keeps its location in the surfactant adsorption layer, decreasing the electrostatic repulsion between the bubbles, so the foamability depends mostly on its concentration. Regarding Li^+ counter-ions, which have mostly an electrostatic screening effect, their presence in the concentration range of 5.5 mmol/L to 20 mmol/L does not affect the foamability of the system, but at 40 mmol/L the foamability is suddenly increased significantly at the lowest absolute value of the surface potential. This is possibly due to the faster surfactant adsorption due to the decrease in the surface potential. In the case of Na^+ counter-ions, the foamability is lower than in the case of LiCl, due to the lower surface potential; however, here again the foamability does not depend on the concentration of NaCl, probably due to the very high turbulence imposing a strong nonequilibrium system.

Let us look at the correlation between the surface potential of the equilibrium foam films and the rate of foam decay.

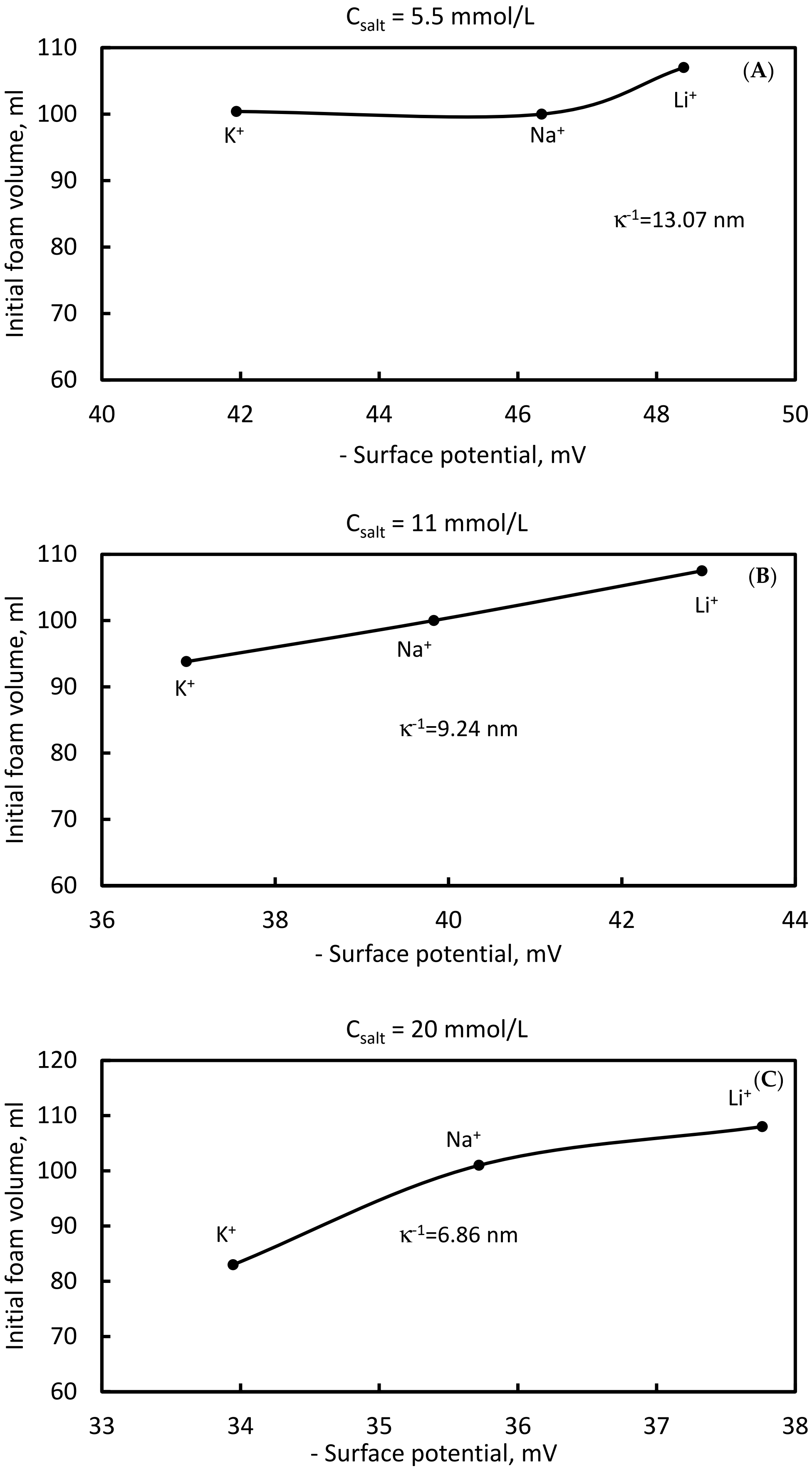

Figure 9. *Cont.*

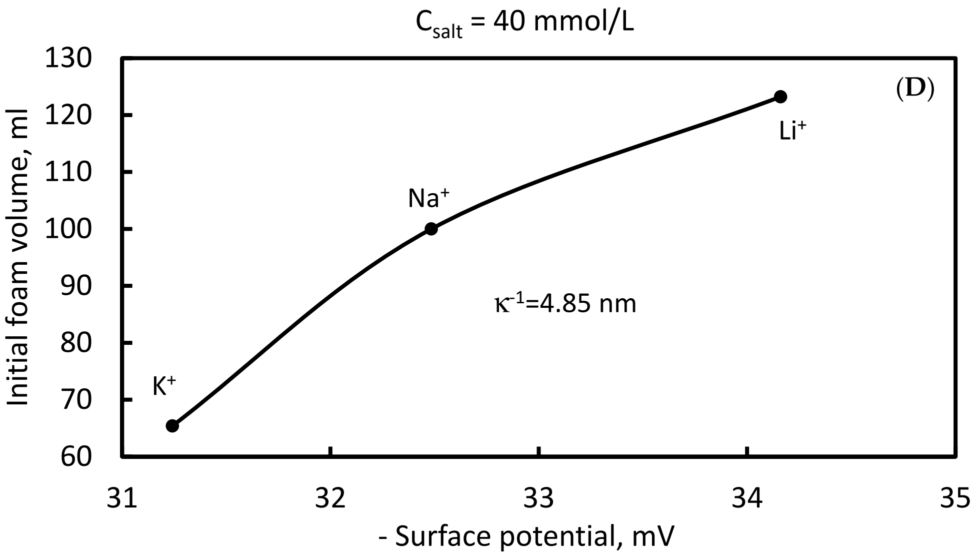

Figure 9. Initial foam volume versus equilibrium surface potential values of the foam films for: (**A**) 5.5 mmol/L added salt; (**B**) 11 mmol/L added salt; (**C**) 20 mmol/L added salt; (**D**) 40 mmol/L added salt. The inverted Debye length for each particular case is presented as well.

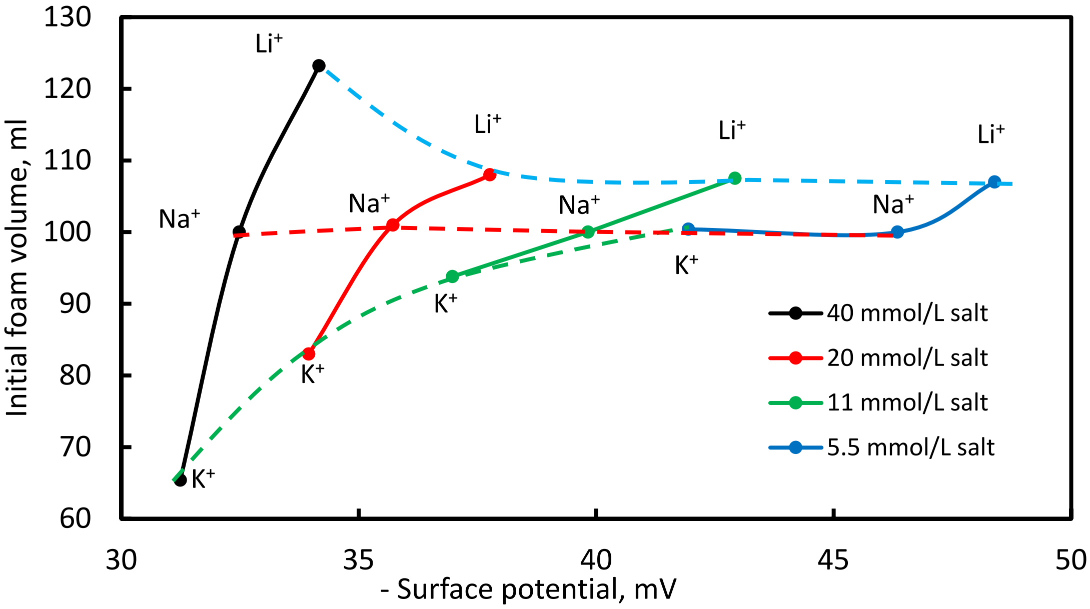

Figure 10. Initial foam volume versus equilibrium surface potential values of the foam films for all of the concentrations of the added salt.

Figure 11 presents the initial rate of foam decay versus the surface potential values of the equilibrium foam films for each one of the concentrations of the added salts. In all of the cases, the initial rate of foam decay increases with the increase in the absolute value of the surface potential and vice versa. Foam with more charged electrostatic bubbles decays faster and vice versa. During the generation of the foam at the high turbulence of shaking, the system is far away from equilibrium. Under such a dynamic regime, the adsorption layers of SDS are less populated by surface-active co-ions. For this reason, the electrostatic repulsion between the bubbles controls the foamability. We will call this phenomenon a regime of electrostatic stabilization. After the termination of the shaking, the foam is already produced and the system starts tending to equilibrium, which is related to the significant rate of adsorption of the surface-active DS$^-$ co-ions. The more charged bubbles will have a slower rate of adsorption of DS^- co-ions due to the larger electrostatic barrier and vice versa. Hence, foam with more charged bubbles will decay faster and vice versa. We call this phenomenon the regime of electrostatically controlled surfactant adsorption.

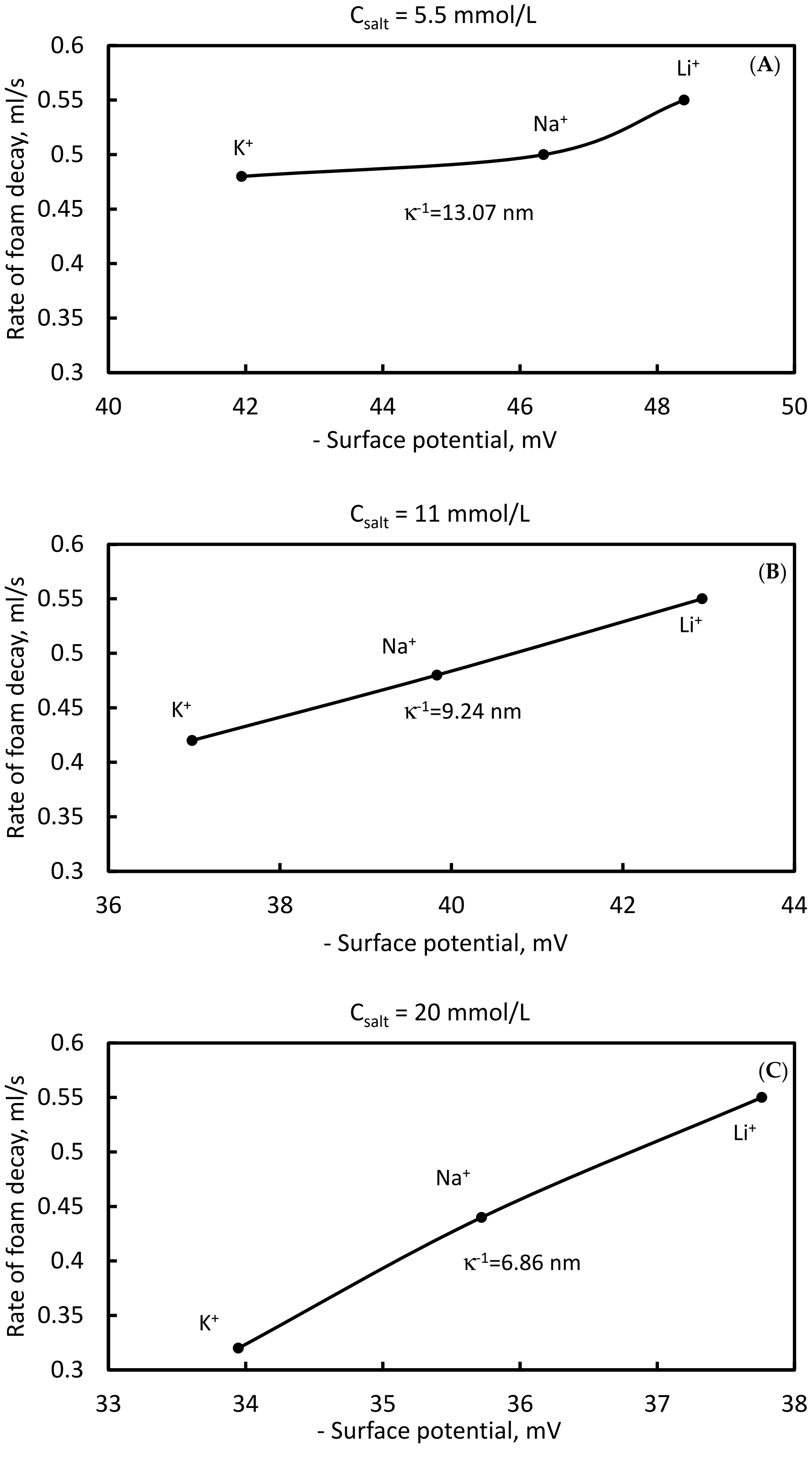

Figure 11. *Cont.*

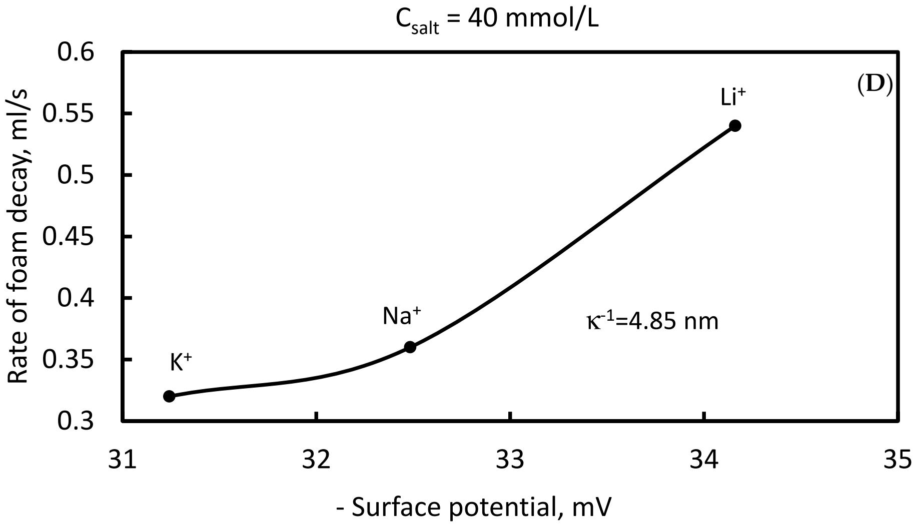

Figure 11. Initial rate of foam decay versus equilibrium surface potential values of the foam films for (**A**) 5.5 mmol/L added salt; (**B**) 11 mmol/L added salt; (**C**) 20 mmol/L added salt; (**D**) 40 mmol/L added salt. The inverted Debye length for each particular case is presented as well.

Figure 12 presents the initial rate of foam decay versus the value of the surface potential of the equilibrium foam films at each one of the concentrations of added salts. It allows one to follow the counter-ion-specific effect along with the surface potential on the rate of foam decay. Similarly, Figure 11 shows that the initial rate of foam decay decreases with the decrease in the absolute value of the surface potential, as discussed above and vice versa. Interestingly, one can see that the Li^+ counter-ion does not affect the rate of foam decay in the whole concentration range of added salt. We have already concluded that in the case LiCl, the electrostatic screening is the only effect because Li^+ counter-ions practically do not adsorb on the surfaces of the bubbles, keeping the largest possible charge of the bubbles. Evidently, the characteristic time for adsorption of DS^- co-ions of the surfaces of the bubbles after termination of the shaking is longer than for the foam decay. For comparison, the Na^+ counter-ion accumulates on the surface of the bubbles, decreasing their charge and allowing faster adsorption of the DS^- co-ions on the bubbles. One can see that the rate of foam decay in the case of added NaCl is slower than in the case of LiCl. The larger the concentration of NaCl, the smaller the absolute value of the surface potential and the rate of foam decay. Similarly, the stronger effect of K^+ counter-ions is due to its large specific energy of adsorption on the surfaces of the bubbles. With KCl, the system reaches a minimum rate of foam decay at 20 mmol/L and 40 mmol/L KCl.

Figures 9–12 give information about how the type of the ion and the surface potential affect the initial foam volume and the initial rate of foam decay. However, our concept for foam production should be mostly indicative of our system.

Figure 13 presents the foam production versus the surface potential of the equilibrium foam films at each one of the concentrations of the added salts. One can see that the foam production value increases upon the decrease of the absolute value of the surface potential and vice versa. In the case of 40 mmol/L added salt, KCl makes an exclusion expressed in the sudden drop of the foam production at the smallest possible absolute value of the surface potential, which is an indication of its converting into a foam suppressor. This could be due to the beginning of precipitation of this surfactant, causing a decrease in the surfactant concentration. Figure 13, which unifies both foamability and foam durability, indicates that the regime of electrostatically controlled surfactant adsorption is mostly important for foam production. The smaller electrostatic charge of the bubbles contributes to faster adsorption of DS^- co-ions on the bubbles, boosting foam production.

Figure 14 presents the foam production versus the surface potential of the equilibrium foam films at each one of the concentrations of the added salt. One can see again here that within the same concentration of the added salt, the foam production increases upon the reduction of the absolute value of the surface potential. One can see as well that in the case of LiCl, the presence of Li^+ counter-ions has no effect on the foam production in the concentration range of 5.5 mmol/L to 20 mmol/L, but at 40 mmol/L LiCl, a sudden significant increase in the foam production is registered. Indeed, as mentioned above, Li^+ counter-ions almost do not adsorb on the bubbles, thus keeping the highest possible absolute value of the surface potential, which results in the lowest foam production among the three salts. In the case of NaCl, the increase in its concentration boosts the foam production due to its adsorption on the bubbles, thus reducing their electrostatic charge, resulting in a faster rate of adsorption of the DS^- co-ions. Indeed, the foam production in the case of NaCl is larger than with LiCl. The strongest booster of foam production is KCl because K^+ counter-ion adsorbs mostly on the bubbles, thus reducing mostly their electrostatic charge, resulting in the fastest rate of adsorption of DS^- co-ions. It has the largest foam production value among the three salts, excluding the case at 40 mmol/L KCl, at which it converts into a foam suppressor.

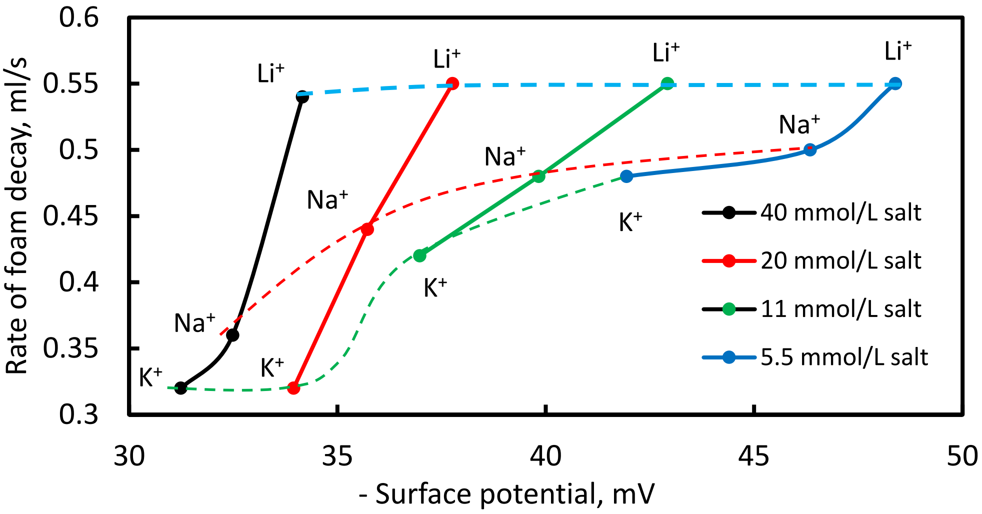

Figure 12. Initial rate of foam decay versus equilibrium surface potential values of the foam films for all of the concentrations of the added salt.

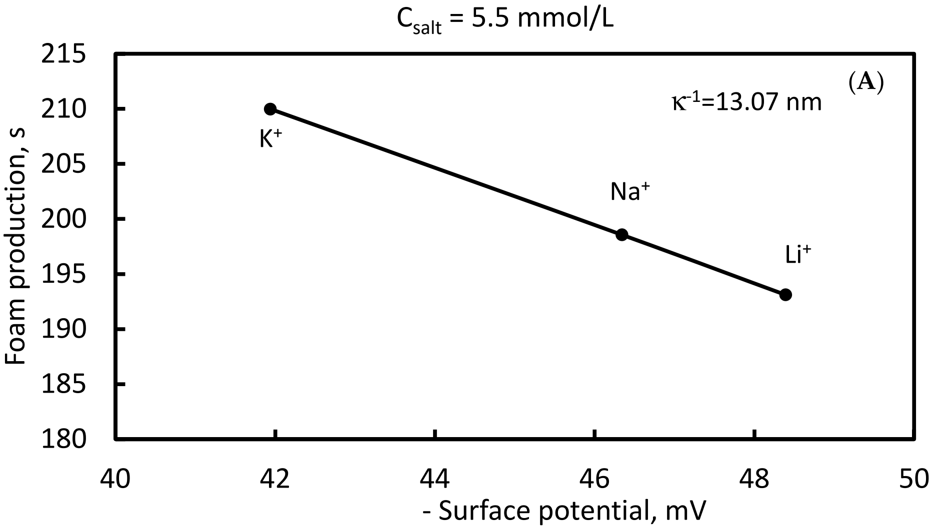

Figure 13. *Cont.*

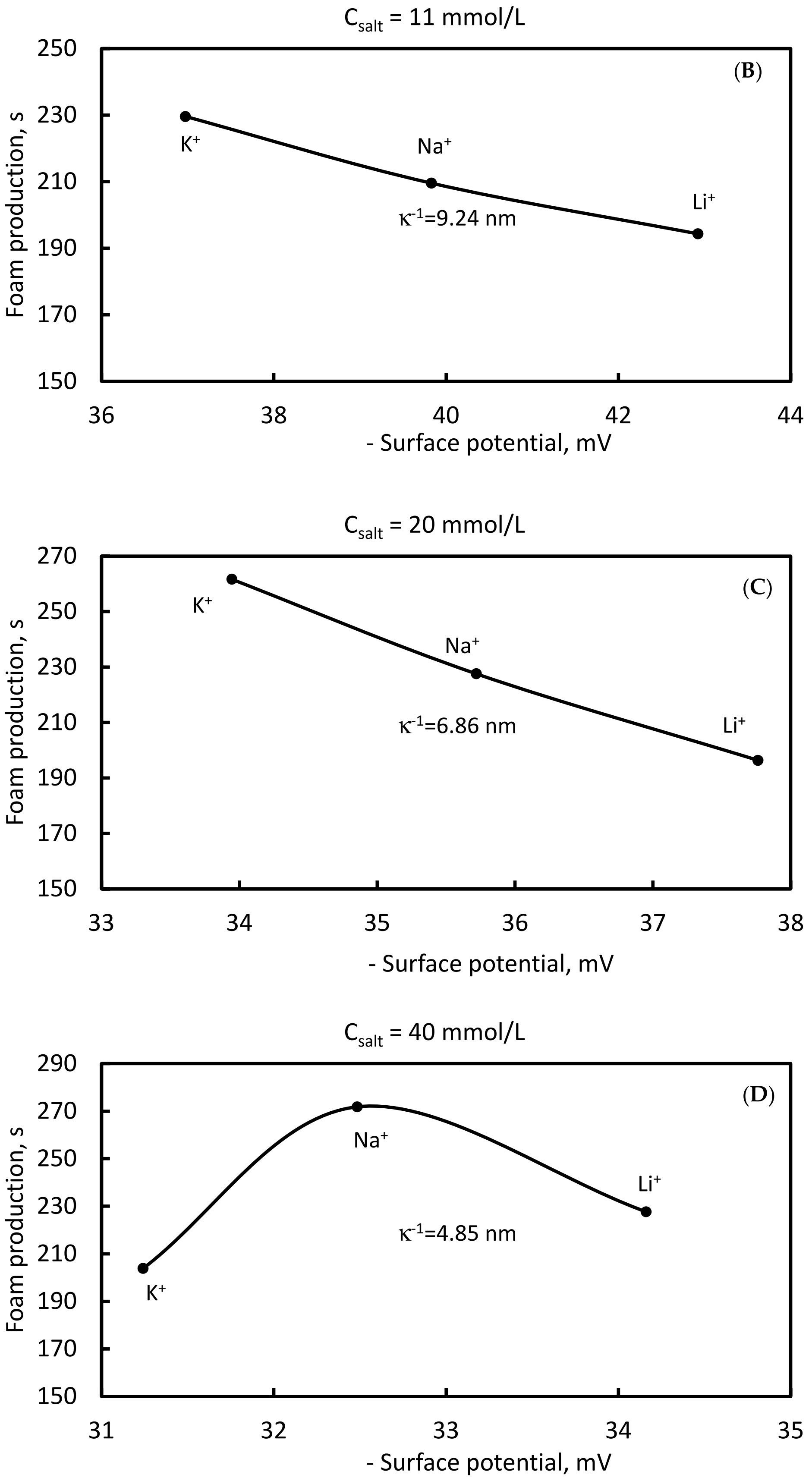

Figure 13. Foam production versus equilibrium surface potential values of the foam films for: (**A**) 5.5 mmol/L added salt; (**B**) 11 mmol/L added salt; (**C**) 20 mmol/L added salt; (**D**) 40 mmol/L added salt. The inverted Debye length for each particular case is presented as well.

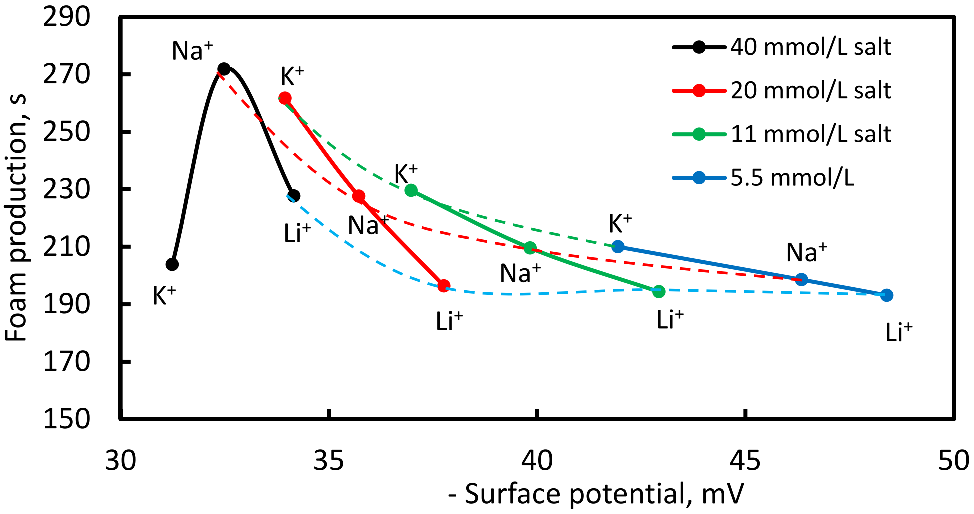

Figure 14. Foam production versus equilibrium surface potential values of the foam films for each one of the concentrations of the added salt.

4. Discussion

The experiment on the foam films stabilized by 0.5 mmol/L SDS in the presence of added LiCl, NaCl and KCl in the concentration range of 5.5 mmol/L to 40 mmol/L allowed us to calculate the surface potential of the equilibrium films at each particular concentration of added salt by means of DLVO theory. The results show that the type of the counter-ions is important for the value of the film thickness and, consequently, for the value of the surface potential. Each type of counter-ion has its own specific energy of adsorption on the bubbles, thus affecting their surface potential and, consequently, the electric charge. The surface potential of the equilibrium foam films is correlated by means of a linear dependence on the specific energy of adsorption of the Li^+, Na^+ and K^+ counter-ions. The smallest specific adsorption energy on the air/water interface belongs to Li^+ counter-ions. It was shown that it practically does not adsorb on the surface of the bubbles. Hence, their effect is due only to the electrostatic screening, reducing the surface potential. For this reason, it gave the highest possible absolute value of the surface potential among the three types of counter-ions. For comparison, Na^+ and K^+ counter-ions have both a screening effect and a counter-ion effect by means of their additional adsorption on the bubbles. The maximal counter-ion effect reducing mostly the absolute value of the surface potential belongs to K^+ counter-ion followed by Na^+ and Li^+ counter-ions.

A correlation between the specific energy of adsorption of the counter-ions and the foamability, the rate of foam decay and the foam production for each particular concentration of the added salt was developed. A correlation between the surface potential of the equilibrium foam films and the same three parameters of the foam was also developed. The two types of correlations comply with each other. In general, the foamability of each system is controlled by the regime of electrostatic stabilization of the bubbles. The largest electrostatic stabilization corresponding to the highest value of the surface potential is with the counter-ions with the smallest specific energy of adsorption Li^+, followed by Na^+ and K^+ counter-ions. The foam production is the most indicative parameter expressing the quality of the foaming system. It is governed by the regime of electrostatically controlled surfactant adsorption.

5. Conclusions

The numerical values of the surface potentials of the equilibrium foam films for each of the cases and the corresponding specific counter-ion adsorption on the film surfaces are presented in Table 1.

Table 1. Surface potential values of equilibrium foam films stabilized by 0.5 mmol/L sodium dodecyl sulfate + added salt in the concentration range of 5.5 mmol/L to 40 mmol/L with the corresponding values of specific energy of counter-ions adsorption of Li^+, Na^+ and K^+ counter-ions at T = 293.15 K; the surface potential values with the excluded ion-specific effect ($u_0/k_BT = 0$) calculated from Figure 4 are presented as well.

C_{salt}, mmol/L	$-\varphi_s$ (No Spec. Effect), mV	$-\varphi_s$ (LiCl), mV	$-\varphi_s$ (NaCl), mV	$-\varphi_s$ (KCl), mV
5.5	49.04	48.39	46.34	41.94
11	42.95	42.92	39.83	36.97
20	37.75	37.76	35.72	33.95
40	34.10	34.16	32.48	31.24
Type of counter-ion	N/A	Li^+	Na^+	K^+
$-u_0/k_BT$	0.00	0.09	0.33	0.90

One can see in Table 1 that the values of the surface potential in the case of added LiCl are very close to the case of no ion-specific effects, at which $u_0/k_BT = 0$. In addition, the larger the absolute value of u_0/k_BT, the smaller the absolute value of the surface potential is and vice versa. During its generation, the foam is far from equilibrium, but correlations with equilibrium foam films can still be made.

Generally the following contributions of our work can be drawn:

1. A correlation between the foamability, the initial rate of foam decay, the foam production and the specific energy of adsorption of the counter-ions and the related absolute values of the surface potential of the equilibrium foam films is developed for the first time in the literature. One can see that most of the correlations are either linear or close to linearity.
2. It was reported for the first time that the Li^+ ions practically do not adsorb on the air/water interface. Thus, the effect of these counter-ions is only electrostatic screening. In reality, the addition of electrolytes always screens the electrostatic interaction between the bubbles, by means of an effective decrease in the surface potential and the shrinking of the diffusive layer of counter-ions [38,46] due to the overall decrease in the energy of the electrostatic field because of its interaction with the counter-ions.
3. The counter-ion effect on the foamability and the rate of decay of foam, produced by means of the Bartsch method, was studied separately for the first time. The counter-ions, in a sequence of increasing foaming effect, can be ordered as follows: $Li^+ > Na^+ > K^+$. The generation of foam occurs under the regime of electrostatic stabilization of the bubbles. These bubbles are produced during the foam generation and their electrostatic repulsion hinders their coalescence, thus boosting foamability. On the contrary, the counter-ions in the sequence of increasing the foam stabilization effect can be ordered as followed: $Li^+ < Na^+ < K^+$. The decay of the foam occurs under the regime of electrostatically controlled surfactant adsorption. Immediately after the generation of the foam, the vigorous adsorption of surface-active co-ions on the bubbles begins. The bubbles in the presence of counter-ions with the largest absolute value of the specific adsorption energy of counter-ions will have the smallest electrostatic barrier preventing the surfactant adsorption and the bubbles will undergo the fastest surfactant adsorption, causing the slowest foam decay. The opposite happens with the bubbles in the presence of counter-ions with the smallest absolute value of the specific energy of adsorption of the counter-ions.

These results allow one to better understand the counter-ion-specific effect on foamability and the subsequent foam durability of aqueous solutions of ionic surfactants.

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