A Comprehensive Analysis of Selected Anionic Surfactants Behaviour in Aqueous Systems Containing Metal Ions and Inorganic Acid

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Abstract: The influence of co-ions on the adsorption properties of two surfactants: ABS (dodecylbenzene sulfonic acid) and its sodium salt ABSNa50 in the aqueous systems, has been studied and discussed. On the basis of experimental measurements of equilibrium and dynamic surface tension, a series of parameters were determined, such as critical micelle concentration (CMC), adsorption parameters, diffusion coefficients, and the micellar dissociation constant. It was proved that values of CMC vary according the contents of accompanying metal ions (zinc(II), copper(II), cobalt(II), nickel(II)) and hydrochloric acid in the system under discussion. Moreover, it was found that as the concentration of surfactant in the system increases, the estimated values of the diffusion coefficients decrease. The obtained results indicate the need to analyse the basic surface properties of surfactants in case of their application in the systems containing additional substances.

Keywords: dodecylbenzene sulfonic acid; sodium dodecylbenzene sulfonate; surface tension; adsorption; heavy metals; hydrochloric acid

1. Introduction

Surfactants, due to their unique properties, reduce surface tension, adsorb at the interface, and self-aggregate. Due to these properties, these compounds are utilized in daily life and industry, as well as in natural processes. On the one hand, they are essential for breathing (pulmonary surfactants), and on the other hand, they are used as detergents [1,2]. The widespread use of these types of compounds means that they are often present in aquatic systems and should be examined in a wide range. The surface activity of this group of compounds depends on several factors. First, the structure of the surfactants and, in particular, the interactions between the hydrophobic and hydrophilic groups should be considered. Therefore, it is important to test a wide range of surfactants. Moreover, the other conditions such as electrolyte additive, pH, temperature, etc. affect surfactant properties in solution. For example, surface activity of the surfactants will depend on the metal ionic content in the system. These ions bind to surfactant molecules. Studies indicate that these interactions depend on charges, size, ion specific effect, and coordination ability. Therefore, on the basis of the studies carried out for one metal, it is not possible to generalise the results for a whole range of salts [3]. These effects have been studied and described in the literature for several surfactants and associated salts, such as the anionic surface activity compounds: sodium dodecyl sulfate (SDS) [4–7] and N-lauroylsarcosine sodium salt [7], the cationic surfactants: alkyltrimethylammonium bromids [8] and hexadecyltrimethyl-ammonium bromide [5], the amphoteric surfactant: cocamidopropyl betaine [9] and the nonionic surfactants: OP-10 [10] and polyoxyethylene nonylphenyl ether [11,12].

As follows from the investigations presented above, the influence of metal ions, as well as other substances, on the surfactants micellization behaviour is important and should be studied in more detail. These studies are essential not only for the cognitive effect but also for the application. There are a number of applications for such systems that contain surfactants and metal ions, for example, cloud point extraction [13–15], micellar enhanced ultrafiltration [16–18], ion exchange [19,20], bitumen emulsion technology [21], leaching [22], continuous countercurrent foam separation [3,11] and flotation in mineral processing [23–25], as well as adsorption using surfactant-modified beads [26] and polymer–surfactant aggregates [27] or selective precipitation in the presence of surfactants [28]. It should be also noted that the extensive use of both surfactants and metals also contributes to their presence in wastewater. Here, knowledge of the interactions between these components can provide a fundament for the development of efficient separation methods [29]. It seems important, especially with such a wide presence of surfactants, to assess their surface properties, especially in the presence of other substances that are assumed to alter the properties of the compounds analysed.

The surfactant market is still a dynamically changing industry (with the Compound Annual Growth Rate, it equals to 5.8% during 2019–2025 [30]). It must respond to changing customer needs and preferences. When analysing the global economy, it should be borne in mind that surfactants, long-known as well as introduced to the retail market not long ago, are used in many areas of life. This is not always the original purpose as foreseen by the manufacturer that is currently used. Thus, it is not always possible to anticipate all the necessary tests that are needed to characterise a product. Despite the knowledge of potential changes in these properties, there is still a lack of comprehensive research. Moreover, due to the number of surfactants present on the market as well as the possibility of their use, it is not possible to carry out a sufficient number of tests in full scope.

In terms of market analysis, anionic surfactants, just next to the non-ionic ones, are the largest group produced and, consequently, also used. This group includes linear alkylbenzene sulfonate (LAS), alpha olefin sulfonates (AOS), secondary alkane sulfonate (SAS), and methyl ester sulfonates (MES). Therefore, in this paper, the commercial anionic surfactant ABS acid (dodecylbenzene sulfonic acid, known as LABSA or DBSA, linear alkyl benzene sulfonic acid) and its sodium salt (sodium dodecylbenzene sulfonate, ABSNa50, SDBS) were analysed. These surfactants are very often used in formulations to clean different surfaces due to their good dispersing, emulsifying, wetting, and foaming properties [31]. Furthermore, these compounds are used by other researchers, such as a few examples of the work from 2022 [32–40]. Moreover, because of its acidic structure, ABS could be used in formulations with acidic pH. According to the information provided by the manufacturer, ABS is used as a laundry detergent, as well as in industrial applications including metal cleaning, as an additive for fire-resistant hydraulic fluids and fertilizers, and in emulsion polymerization reactions. This surfactant is applied in the synthesis as a surfactant-type acid catalyst, i.e., in esterification of acids with alcohols in the water medium [41]. Thus, owing to its ability to create high and stable foam, ABSNa50 is recommended for the products where foam is essential and necessary. In addition, it has excellent detergency, degreasing, wetting, dispersing, and emulsifying properties as well as great resistance to hydrolysis in the alkaline environment. These properties cause these surfactants to be used as components in washing and cleaning detergents for household and professional use, air-entraining admixtures in the construction industry, plant protection products, car chemistry, and in emulsion polymerization. Moreover, both of the surfactants are biodegradable, which is an essential fact from a practical and ecological point of view.
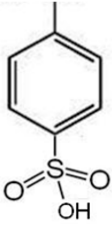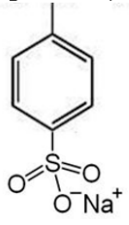
Since earlier studies in the group had shown a significant correlation between surface properties and metal ions and acid present in aqueous medium in the case of a modal surfactant—SDS [4], it seems important to investigate commercially available surfactants in this area. Therefore, taking into account the information presented above, the objective of this paper was to investigate the influence of type of metal ions and presence of HCl in various concentrations on the surface properties (CMC, adsorption parameters, and

dynamic surface tension) of the two commercial anionic surfactants ABS and ABSNa50. Although ABS and ABSNa50 are widely used, interactions with other compounds in aqueous media are poorly explored.

2. Materials and Methods

There were two commercial anionic surfactants applied: ABS acid (dodecylbenzene sulfonic acid; CAS number: 85536-14-7; IUPAC name: 4-(tridecan-3-yl)benzene-1-sulfonic acid), and for comparison sodium salt ABSNa50 (sodium dodecylbenzene sulfonate (C10-13 alkyl derivatives); CAS number: 68411-30-3; IUPAC name: sodium 4-undecylbenzenesulfonate), purchased from PCC Exol SA, Brzeg Dolny, Poland (Table 1). They were used as received, without any purification. This approach was intended to study the compounds and their interactions as they are commonly used.

Table 1. Characterization of anionic surfactants, based on the information from the manufacturer's brochures.

Surfactant	Dodecylbenzene Sulfonic Acid	Sodium Dodecylbenzene Sulfonate
Alternative names	dodecylbenzenesulfonic or benzenosufonic acid, 4-C10-13-sec-alkyl derive, linear alkyl benzene sulfonic acid (LABSA)	sodium salts, C10-13 alkyl derivatives, benzenesulfonic acids
Abbreviation	ABS	ABSNa50
Type	anionic	anionic
Structure	$CH_3 - (CH_2)_x - CH_2 - CH - (CH_2)_y - CH_3$ (4-substituted benzene ring with SO_2OH group)	$CH_3 - (CH_2)_x - CH_2 - CH - (CH_2)_y - CH_3$ (4-substituted benzene ring with $SO_2O^- Na^+$ group)
Molecular weight (g/mol)	approx. 320	340–348
Density (20 °C) (g/mL)	1.06	1.07
Form of occurrence	light brown to dark brown liquid	liquid
Odour	characteristic	weak, characteristic
Properties	dispersing, emulsifying, wetting, and foaming properties	dispersing, emulsifying, and wetting properties
Application	metal cleaning, laundry, cleaning detergents for the household and professional use, production of hydraulic fluids (fire resistant), production of textiles, plant protection products	agrochemicals, pesticides, fertilizers, industrial cleaning and washing, detergents, paints and varnishes, lubricants and functional fluids, construction industry, drilling and tunneling, metallurgical industry, machining, mining industry, oil and gas extraction, textiles

Four inorganic salts: $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$ were used as a source of metal ions, while hydrochloric acid was used as an acidic regulator. These chemicals were of analytical grade, purchased from Avantor Performance Materials Poland SA (Gliwice, Poland).

All solutions were made by weighed masses with the accuracy of ± 0.01 mg using water from Elga PURELAB Classic (ELGA LabWater, High Wycombe, UK) with the resistivity = 18.2 MΩ·cm. Pure water or solutions containing metal ions (100 mg/L) and HCl

(0.1–6 mol/L HCl) were applied as the solvent for the preparation of appropriate surfactant solutions. Subsequent solutions were obtained by successive dilutions.

The surface tension measurements were performed using a Krüss (K-12) tensiometer (Krüss GmbH, Hamburg, Germany) with a platinum ring, at room temperature (298 K). The three-time measurements accuracy was ±0.05 mN/m. The CMC was estimated in the typical way, as a point of intersection by fitting the pre-micellar and post-micellar data of the surface tension isotherm. The relationship between surface tension and surfactant concentration in the case of the formation of micelles in the solution can be presented as:

$$\gamma(c) = -A(\ln(CMC) - \ln(c))g(c) + \gamma_{CMC} \tag{1}$$

where g(c) = 1 if c ≤ CMC and 0 if c > CMC, A is the slope of $\gamma = f(\ln(c))$, and γ_{CMC} is the surface tension at the concentration above CMC.

The adsorption parameters of surfactants were calculated using the Szyszkowski equation. The DST measurements were performed with the bubble method (SITA Messtechnik t60 tensiometer (SITA Messtechnik GmbH, Dresden, Germany)) according to the procedure described in [4]. The measurements made it possible to estimate the value of the diffusion coefficients and the micellar dissociation constants and consequently, to determine whether the diffusion affects the ABS and ABSNa50 adsorption.

3. Results and Discussion

### 3.1. Determination of CMC and Adsorption Parameters

The CMC value is a crucial parameter describing each micelle-forming compound. Therefore, its determination is very important. CMC depends mainly on compound structure, type of solvent used, the presence of other substances, mainly strong electrolytes, and the temperature. The basic parameters describing surface activity of the anionic surfactant (AS) were estimated from surface tension measurements [33]. The CMC values were obtained using the relationship between surface tension (γ) versus the logarithm of ABS concentration in the aqueous solutions e.g., the water–AS, water–AS–M(II)) and hydrochloric acid (HCl–AS, HCl–AS–M(II), where AS—anionic surfactant) systems. The representative plots of γ versus log c applied for the determination of CMC are shown in Figure 1a–f (ABS).

The relations shown in Figure 1a–f have a typical shape that indicates the formation of micelles in the solution according to the Equation (1). Furthermore, Figure 1g,h shows a comparison of the CMC values obtained, taking into account the effect of both the concentration of hydrochloric acid and the type of heavy metal ion used. As can be seen, the nature of the figures obtained in the radiation diagram indicates a much greater effect of the HCl concentration than of the type of metal ion on micelle formation in the system containing the ABS surfactant. The figures are not only similar, but also the result of the integration of the areas showed a much smaller variance in the case of Figure 1h (0.122 and 3.67×10^{-3}, for (g) and (h), respectively).

The determination of the CMC value for the system containing ABS surfactant was presented and compared with the ABSNa50 one for which the CMC results were presented in our previous paper [19] (Figure 2).
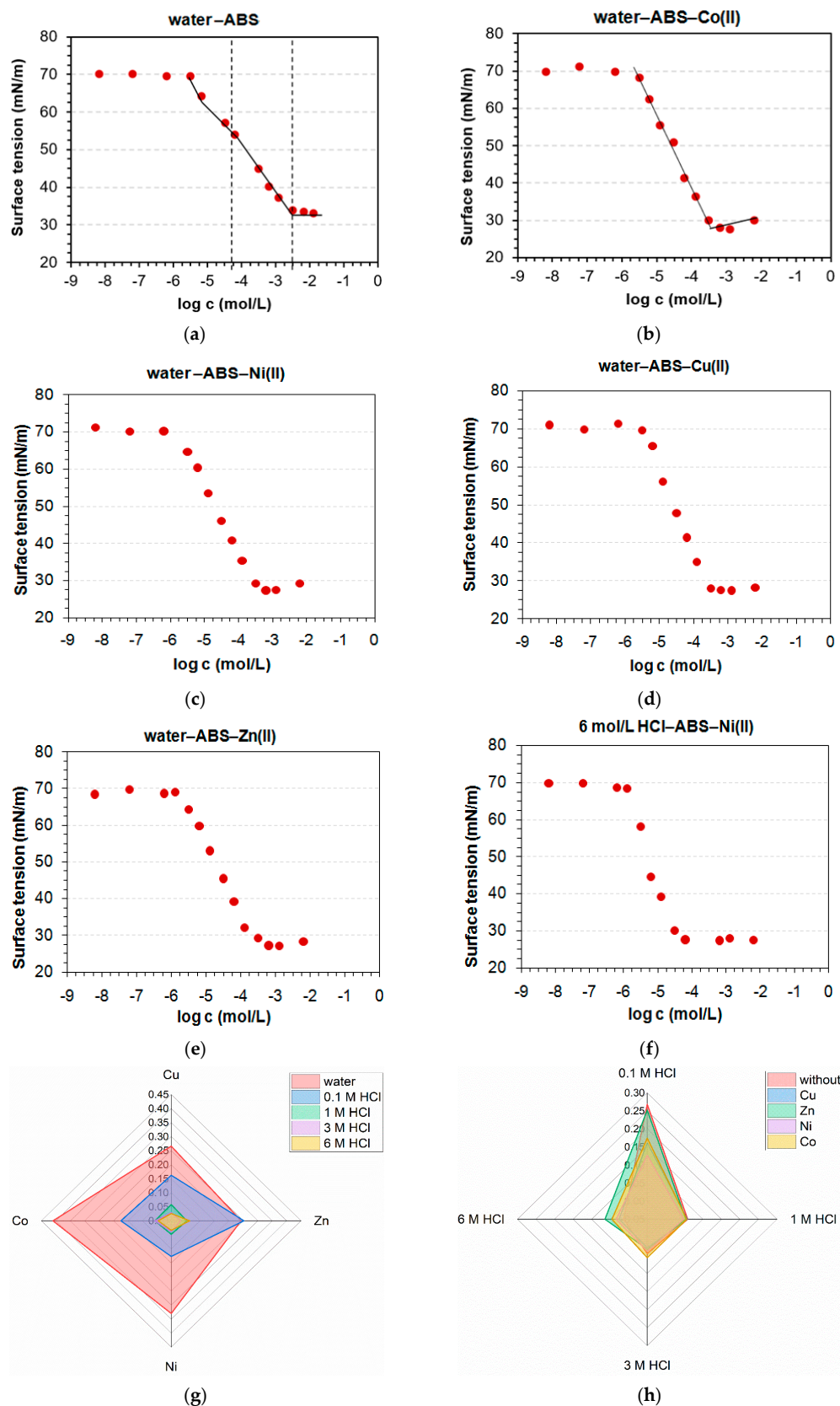
Figure 1. The adsorption isotherms for the ABS surfactant without (**a**) and with (**b**–**f**) heavy metals in water (**a**–**e**) and HCl (**f**) systems with constant concentration of heavy metal ions equal to 100 mg/L and effect of HCl concentration (**g**) as well as type of heavy metal ions (**h**) on CMC values.
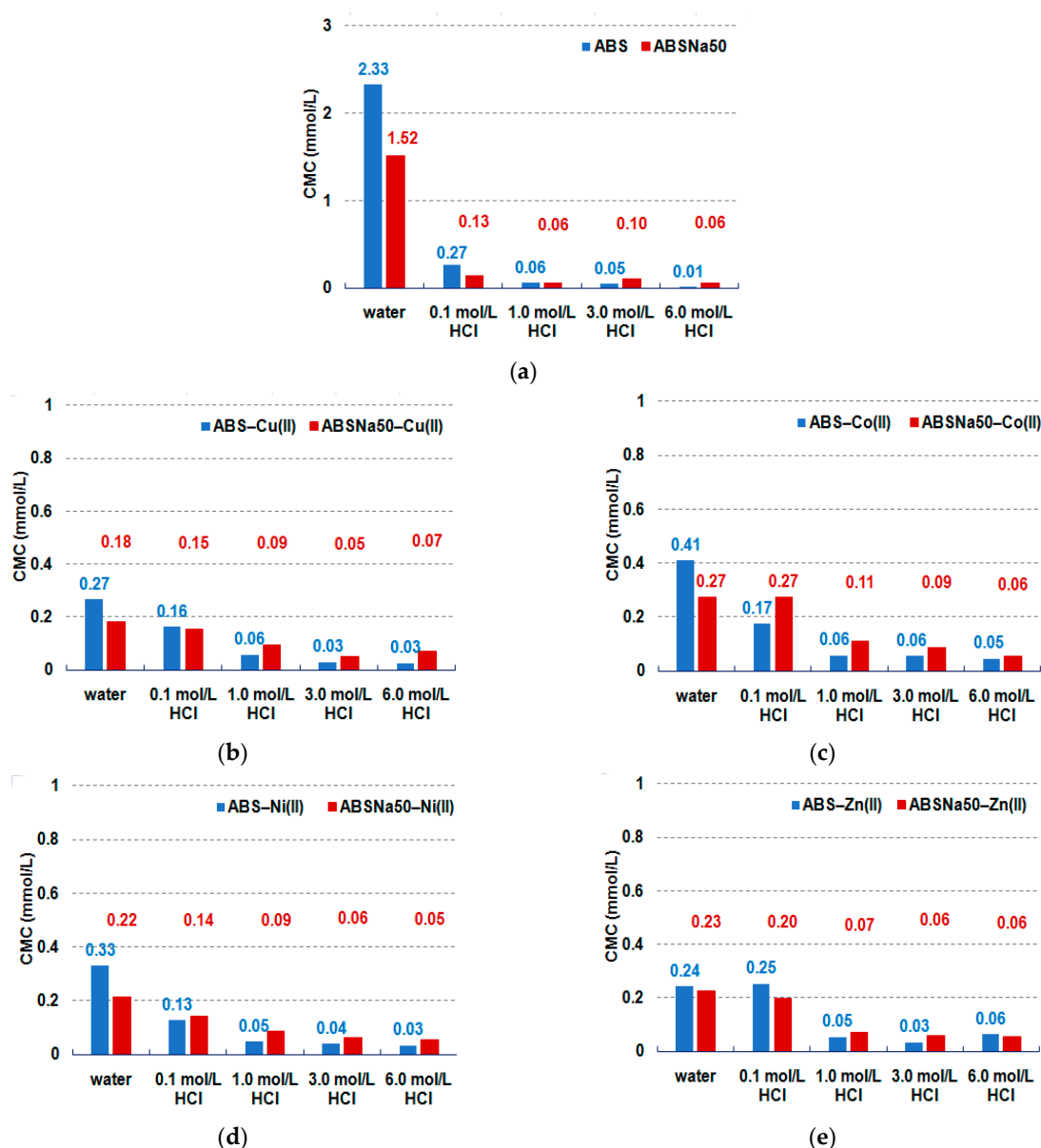
Figure 2. The CMC values comparison obtained for ABS (this paper) and ABSNa50 surfactants for systems without (**a**) and with (**b**–**e**) heavy metals such as Cu(II) (**b**), Co(II) (**c**), Ni(II) (**d**) and Zn(II) (**e**) [19].

The results presented in Figure 2a show that the anionic surfactants show the maximum values of CMC for systems with water (2.33 mmol/L and 1.52 mmol/L, for ABS and ABSNa50, respectively). The obtained results of CMC for ABS in water are greater compared to those presented in the literature (0.385 [42], 0.551 [43], and 1.29 [44] mmol/L) while the values of γ_{CMC} are similar (33.0 in this paper about 33.2 [42] and 32.9 mN/m in [43]). The discrepancies in the presented CMC results are probably due to the various suppliers of surfactants (Sigma-Aldrich, Fluka, and TCI in the cited papers, respectively, and PCC Exol here) and, in consequence, the possibility of applying different procedures for obtaining the compound and impurities after synthesis. Moreover, as mentioned before, the tests presented in this paper were carried out using the commercial preparation without purification to make the results as close as possible to the real conditions. In the case of the sodium salt of ABS, a comparison of the results directly is not available since this is a mixture of different alkyl length acid derivatives (C10–C13). However, the obtained results

are similar to those for the pure compound—sodium dodecylbenzene sulfonate (1.52 in this paper and 1.1 in [45], 2.85 in [46] or 2.73 mmol/L in [47]).

The aggregation of anionic surfactants was investigated taking into account the equilibrium surface tension (γ). In the initial stage, as the concentration of surface-active compound increases, the γ decreases dramatically and then decreases more slowly [41,42], as was presentd for surfactants under consideration in Figure 1. The dramatic decrease of γ is a typical effect, originating from the adsorption of ABS and ABSNa50 molecules at the interface. Moreover, as presented in Figure 1a, the γ–log c plot can be divided into three concentration regions, suggesting a gradual aggregation occurring during the adsorption process. The ABS surfactant in the aqueous solution can form species such as negatively charged soap ($C_{18}H_{29}SO_3^-$), neutral acid ($C_{18}H_{29}SO_3H$), and due to the hydrogen bonds present, also acid–soap dimers [42]. The presence of these compounds in the system, or rather the chemical equilibria present in the dilute solution, which change with increasing ABS concentration, is responsible for the blurring of the first breakpoint and the presence of the second one. With an increase in ABS concentration, the micelles begin to form, and then they are partially transformed into vesicles as a consequence of the acid–soap dimers formation by hydrogen bonding. The shift in equilibrium for high concentrations of ABS is responsible for the formation of micelles and subsequently vesicles due to dimer formation. The acid–soap dimers formation results in the pseudo binary mixed amphiphilic system, which contains a composite of single and double-chained amphiphiles [42,43]. The aggregation behaviour of the ABS surfactant in water could be explained by the dimer mechanism involving hydrogen bonds (Figure 3).
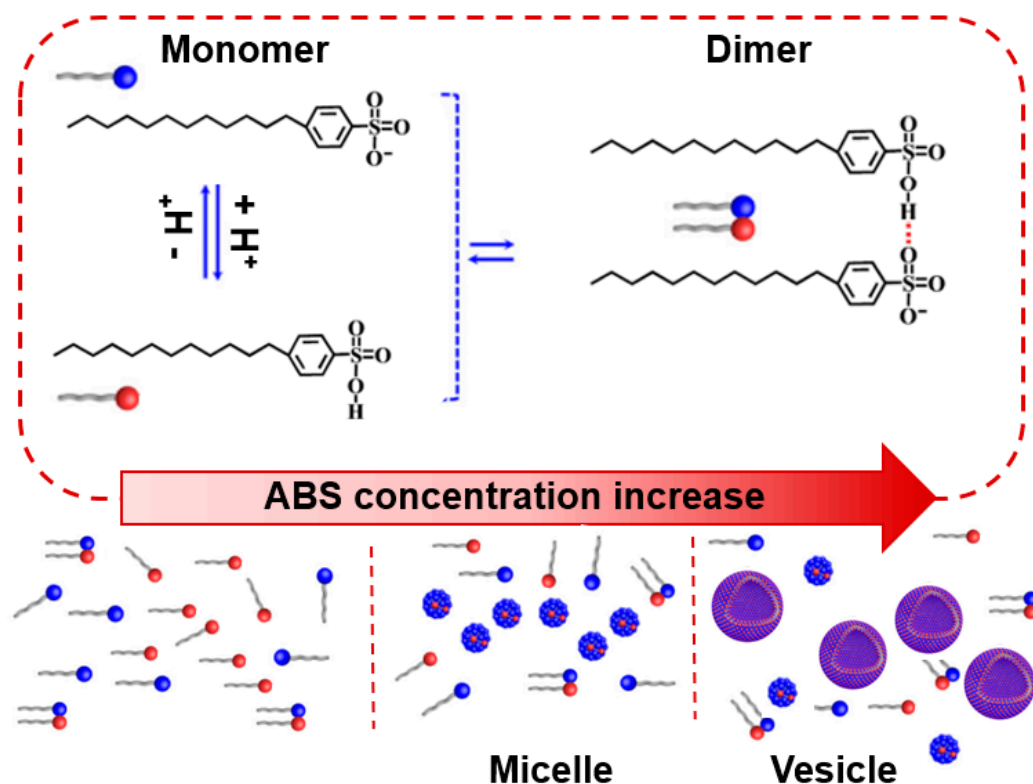
Figure 3. ABS surfactant forms and mechanism of ABS adsorption in the aqueous solutions.

The surfactant aggregation is also greatly influenced by the properties of solvent and coexisting ions. Knowledge about the CMC and the behaviour of surfactants in the hydrochloric acid medium and the presence of heavy metal ions is essential. Finally, anionic surfactants are used to support the removal of metals from wastewater and soil [7,43]. From the results shown in Figure 2 it was found that the presence of both metal ions and HCl changed the CMC values. Regardless of the metal ions, the CMC values in ABS systems

shift toward lower concentrations as the HCl concentration increases. Similar correlations were observed for ABSNa50 [19] and SDS [4]. The resulting relationship is quite different from that of the systems containing ABS and poly(ethylene glycol) as an additive. In this case, the addition of PEG shifts the CMC value towards higher concentrations, which confirms that the surfactant aggregation with PEG causes the formation of small self-assembled micelles. Moreover, the authors showed that with the higher molecular mass of PEG used, the shift of CMC is greater [42]. The shift in CMC to lower concentrations, as well as the decrease in the γ_{min} values obtained in this study (presence of salts and inorganic acid) could be explained by the presence of strong electrolytes in the systems under consideration. The presence of electrolytes promotes the aggregation of ionic surfactants by minimizing the electrostatic repulsions between the hydrophilic main groups of surfactants. This phenomenon results in a tighter packing of molecules, which consequently contributes to the possibility of micelle formation at a much smaller surfactant concentration. In addition, it should be noted that the presence of electrolytes can cause a salt effect accompanied by the displacement of polar surfactant head groups from water into the interface to form micelles. A similar effect of reduction of both the CMC and the minimum surface tension values was observed for sodium dodecylbenzene sulfonate with the addition of NaCl [46] and KCl, NH_4Cl, and $MgCl_2$ [47] or other ionic surfactants, e.g., the cationic surfactant CTAB [48] or SDS [49] with NaCl. This relationship for the systems studied is presented in Figure 4 in the form of the multivariate Kernel density estimation.
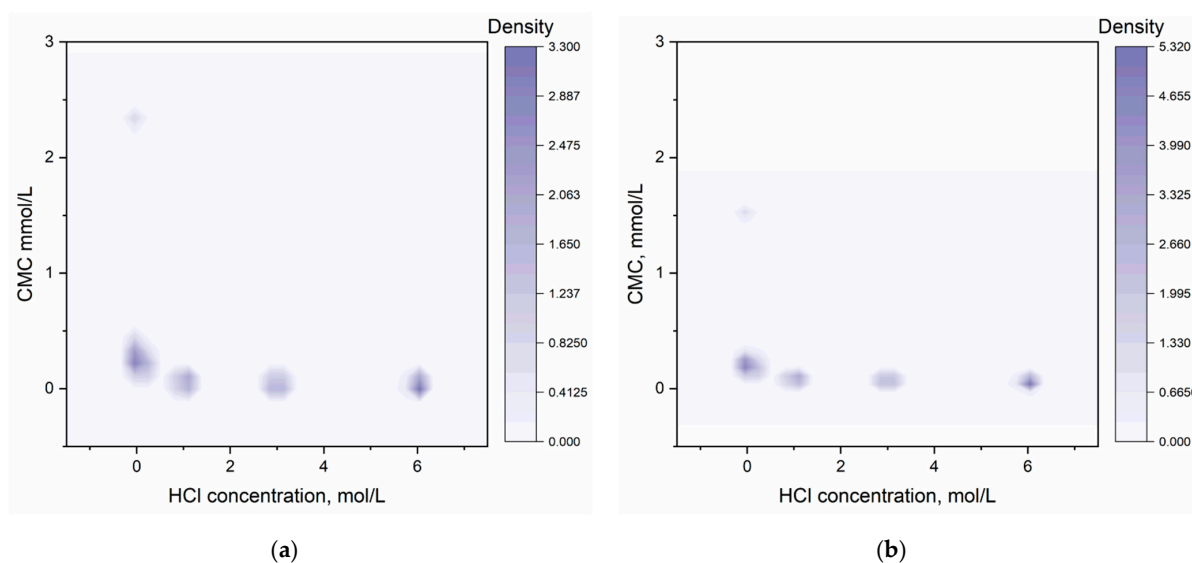
Figure 4. 2D Kernel density graph for (**a**) ABS and (**b**) ABSNa50 surfactants.

The results indicate that the CMC reduction is related to the additional ions in the system that come from the dissociation of acid and their interactions with the surfactants, but the explanation of this phenomenon is not so obvious. It should be noted that as the concentration of HCl increases, a lower scatter of the obtained CMC results for different metal salts is observed. This indicates that the presence of acid determines to a much larger extent the surface behaviour of the analyzed ionic surfactants in comparison to the presence of metal. However, in the case of the aqueous solutions containing only metal salts, a significant difference in the CMC obtained for the Co(II) ions containing systems is observed. In the other cases, the values are similar. This behaviour of the system may be due to the differences in the van der Waals radius (R) (Zn 139 pm, Cu 140 pm, Ni 163 pm, and Co 200 pm) and the same valence (Z). Cations with high Z/R values are more hydrated and can be treated as water structure makers [47]. The aspect of hydration energy is also relevant to the study in question. The adsorption properties of metal ions are closely related to the hydration energy. For the metal ions tested, the values of molar Gibbs energies of hydration of ions are similar (−2010, −1955, −1980, −1915 kJ/mol, for Cu(II), Zn(II) Ni(II), Co(II) respectively [50].

Furthermore, it can be seen from the density graph (Figure 4) that the CMC shift towards the lower concentration occurs up to a certain concentration (about 1 mol/L HCl), after which it remains almost constant, regardless of the metal ion under investigation. This phenomenon can be explained by the achievement of the maximum charge shielding by the counter ions, so the addition of more salt will not cause significant changes. Thus, with the addition of HCl, there will be much fewer monomers in equilibrium with micelles.

The Szyszkowski equation (Equation (2) was applied for the ABS and ABSNa50 adsorption description in the presented system and determination of the other adsorption parameters according to Equations (3)–(6) (Figure 5) [51].
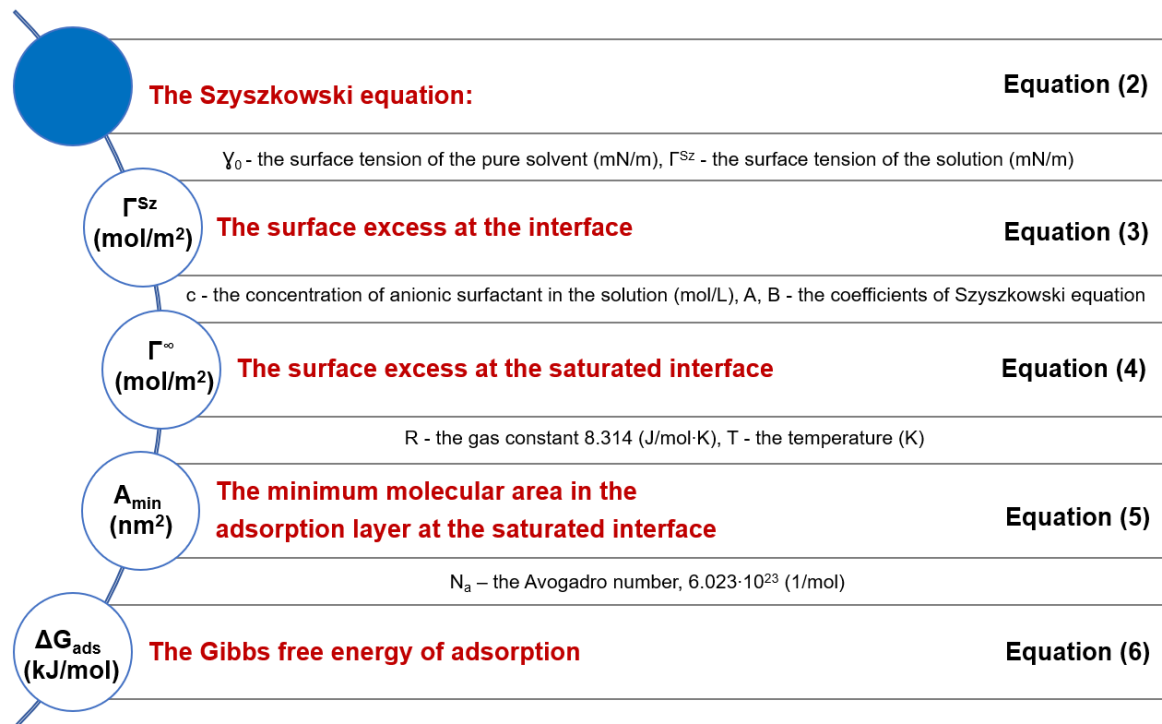
The Szyszkowski equation: — Equation (2)

γ_0 - the surface tension of the pure solvent (mN/m), Γ^{Sz} - the surface tension of the solution (mN/m)

Γ^{Sz} (mol/m²) — **The surface excess at the interface** — Equation (3)

c - the concentration of anionic surfactant in the solution (mol/L), A, B - the coefficients of Szyszkowski equation

Γ^∞ (mol/m²) — **The surface excess at the saturated interface** — Equation (4)

R - the gas constant 8.314 (J/mol·K), T - the temperature (K)

A_{min} (nm²) — **The minimum molecular area in the adsorption layer at the saturated interface** — Equation (5)

N_a – the Avogadro number, $6.023 \cdot 10^{23}$ (1/mol)

ΔG_{ads} (kJ/mol) — **The Gibbs free energy of adsorption** — Equation (6)

Figure 5. Characterization of the parameters used for the ABS and ABSNa50 adsorption.

$$\gamma^{Sz} = \gamma_0 \left(1 - B \ln\left(\frac{c}{A} + 1\right)\right) \tag{2}$$

$$\Gamma^{Sz} = \frac{\gamma_0\, B\, c}{R\, T\, (c + A)} \tag{3}$$

$$\Gamma^\infty = \frac{\gamma_0\, B}{R\, T} \tag{4}$$

$$A_{min} = \frac{1}{N_a \Gamma^\infty} \tag{5}$$

$$\Delta G_{ads} = -RT \ln A \tag{6}$$

The adsorption parameters were determined by the non−linear regression with the support of the MathCad Prime 4.0 program and are presented in Figure 6 and Table 2. The surface excess at the interface (Γ^{Sz}) determines the number of surfactant molecules per unit area of the saturated adsorption layer. The ABS and ABSNa50 molecules accumulated on the surface have a smaller affinity for the intermolecular interactions in the surface layer. From the results presented in Figure 6, for selected systems, it can be observed that Γ^∞ increases sharply with the increasing surfactant concentration and after that the curves reach the plateau, indicating the complete saturation of the phase boundary. Similar relationships were obtained for all the systems analysed. The obtained value of the surface

excess for ABS in water is approximately twice higher than that presented in the paper (2.41 vs. 1.34×10^{-6} mol/m^2) [43]. These differences may result from different origins of the surfactants. In the other cases, comparison of the obtained results is not possible because such results are not available in the literature. In the HCl–AS–Cu(II) systems Γ^∞ (mol/m^2) reaches higher values for higher hydrochloric acid concentration, with the highest values in the systems with 6 mol/L HCl for both surfactants. This increase of Γ^∞ values with more concentrated HCl was not observed for the other heavy metals containing systems (HCl–AS–M(II)) examined in this paper. However, in this case Γ^∞ values are also the highest in the 3 or 6 mol/L HCl systems for cobalt, zinc and nickel.
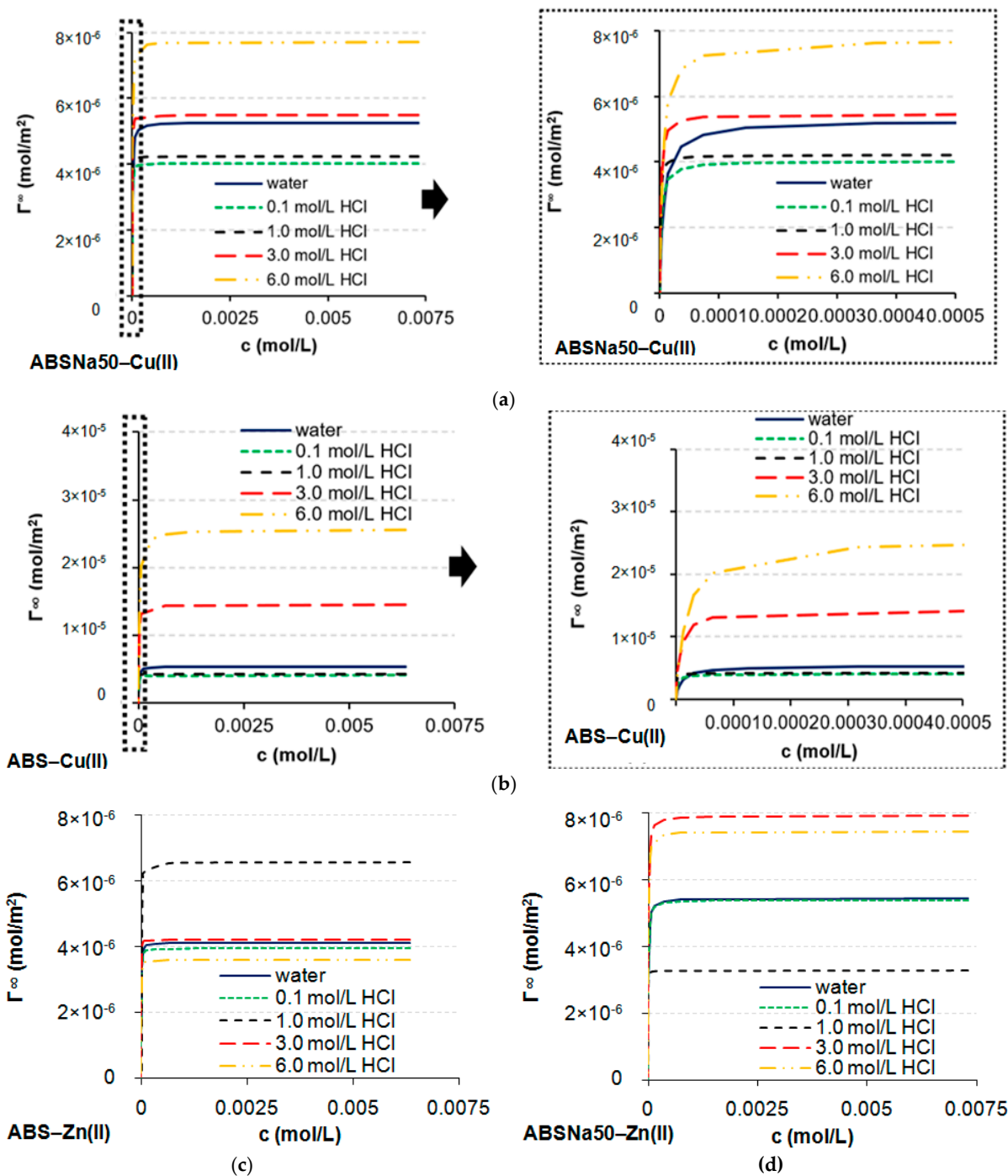

Figure 6. Relations between the Γ^∞ versus concentration of surfactants: (**a,d**) ABSNa50 and (**b,c**) ABS in the presence of Cu(II) (**a,b**) and Zn(II) (**c,d**).

Table 2. Adsorption parameters obtained in the water–AS–M(II)/air or HCl–AS–M(II)/air systems.

Parameters	System without Heavy Metal Ions									
	ABS					ABSNa50				
	Water	0.1 mol/L HCl	1 mol/L HCl	3 mol/L HCl	6 mol/L HCl	Water	0.1 mol/L HCl	1 mol/L HCl	3 mol/L HCl	6 mol/L HCl
$A \times 10^{-6}$	4.64	29.5	2.72	0.044	0.15	6.96	7.58	1.13	1.84	4.54
B	0.085	0.091	0.233	0.091	0.103	0.11	0.228	0.171	0.164	0.265
R^2	0.997	0.980	0.989	0.994	0.934	0.993	0.993	0.934	0.979	0.976
$\Gamma^\infty \times 10^{-6}$ (mol/m^2)	2.41	2.51	6.58	2.60	2.89	3.12	6.28	4.83	4.69	7.43
ΔG_{ads} (kJ/mol)	−30.4	−37.3	−31.7	−42	−38.9	−29.4	−29.2	−33.9	−32.7	−30.5
A_{min} (nm^2)	0.689	0.662	0.252	0.638	0.575	0.533	0.264	0.344	0.354	0.224
System with heavy metal ions										
Co(II)										
$A \times 10^{-6}$	3.67	0.83	2.30	1.60	3.04	9.05	3.03	6.21	1.87	4.88
B	0.135	0.114	0.2	0.138	0.327	0.205	0.155	0.237	0.17	0.283
R^2	0.995	0.995	0.981	0.994	0.987	0.992	0.992	0.99	0.97	0.979
$\Gamma^\infty \times 10^{-6}$ (mol/m^2)	3.90	3.28	5.73	3.89	9.25	5.93	4.46	6.79	4.84	7.86
ΔG_{ads} (kJ/mol)	−31.0	−34.7	−32.2	−33.1	−31.5	−28.8	−31.5	−29.7	−32.7	−30.3
A_{min} (nm^2)	0.425	0.507	0.29	0.427	0.179	0.28	0.373	0.245	0.343	0.211
Ni(II)										
$A \times 10^{-6}$	1.77	0.47	2.12	24.5	2.19	3.28	5.43	2.90	3.57	2.61
B	0.118	0.103	0.216	0.242	0.221	0.15	0.201	0.196	0.25	0.222
R^2	0.998	0.988	0.957	0.997	0.983	0.993	0.996	0.97	0.979	0.979
$\Gamma^\infty \times 10^{-6}$ (mol/m^2)	3.44	2.92	6.25	6.96	6.31	4.38	5.82	5.67	7.19	6.34
ΔG_{ads} (kJ/mol)	−32.8	−36.1	−32.4	−26.3	−32.3	−31.3	−30	−31.6	−31.1	−31.9
A_{min} (nm^2)	0.482	0.569	0.266	0.238	0.263	0.379	0.285	0.293	0.231	0.262
Zn(II)										
$A \times 10^{-6}$	2.56	2.07	2.87	0.55	0.87	6.21	5.46	0.76	5.16	4.21
B	0.142	0.137	0.229	0.153	0.126	0.187	0.187	0.114	0.277	0.267
R^2	0.996	0.997	0.981	0.988	0.974	0.996	0.988	0.951	0.957	0.968
$\Gamma^\infty \times 10^{-6}$ (mol/m^2)	4.14	3.95	6.58	4.21	3.60	5.45	5.40	3.28	7.92	7.45
ΔG_{ads} (kJ/mol)	−31.9	−32.4	−31.6	−35.7	−34.6	−29.7	−30	−34.9	−30.2	−30.7
A_{min} (nm^2)	0.401	0.420	0.252	0.395	0.461	0.305	0.308	0.507	0.21	0.223
Cu(II)										
$A \times 10^{-6}$	8.85	2.34	0.85	7.08	17.2	6.52	2.37	0.85	1.59	4.70
B	0.19	0.144	0.152	0.515	0.908	0.186	0.142	0.152	0.192	0.274
R^2	0.991	0.999	0.993	0.956	0.931	0.985	0.998	0.993	0.959	0.99
$\Gamma^\infty \times 10^{-6}$ (mol/m^2)	5.37	4.08	4.23	14.5	25.6	5.26	4.02	4.22	5.48	7.72
ΔG_{ads} (kJ/mol)	−28.8	−32.1	−34.6	−29.4	−27.2	−29.6	−32.1	−34.6	−33.1	−30.4
A_{min} (nm^2)	0.309	0.407	0.393	0.114	0.0649	0.316	0.413	0.394	0.303	0.215

Moreover, the curves of Γ^∞ (mol/m^2) vs. c (mol/L) for Cu(II) show a steeper shape at the beginning and the plateau of the plot is reached faster with the system containing ABSNa50 than ABS. On the other hand, the Γ^∞ values in the HCl–AS–Cu(II) systems are significantly higher for ABS than ABSNa50 surfactants (3 or 6 mol/L HCl), slightly higher (water–AS–Cu(II)) or at a similar level (0.1 or 1 mol/L HCl). The higher Γ^∞ were generally obtained in the systems containing ABSNa50 than ABS in the presence of cobalt, zinc, and nickel salts.

The values of the ΔG_{ads} are negative in all cases, indicating that the molecules of ABS and ABSNa50 have an excellent ability to adsorb at the interface. These values are usually smaller for the systems with ABS surfactant and the presence of cobalt(II), zinc(II), and

nickel(II) ions than for the systems containing ABSNa50. The more negative values of the Gibbs free energy of adsorption suggest more spontaneous ABS adsorption. The values of ΔG_{ads} are slightly higher or the same for ABSNa50 with Cu(II) systems.

A_{min} is the surface area covered by the adsorbed surfactant molecules at the maximum packing of the molecules. The obtained values of A_{min} in the considered systems are in the range from 0.114 to 0.689 nm^2. The highest vales of A_{min} are found in the systems without HCl and heavy metal ions and may be a consequence of strong repulsion between the same charged heads of the surfactant. For the ionic surfactants A_{min} could decrease with the alkyl chain elongation, nevertheless, this correlation is not a rule, and the additive of other chemicals, such as HCl or heavy metal ions, affects the adsorption parameters [52]. In the presented system with or without heavy metals, the A_{min} is usually higher for ABS than for ABSNa50. The addition of HCl of the increasing concentration as well as heavy metal ions changed the minimum molecular area but the changes were not in one direction. Moreover, the addition of such inorganic compounds could change the equilibrium among electrostatic and hydration interactions, van der Waals forces, and counteract the mutual repulsion between the heads [46].

3.2. Determination of the Dynamic Surface Tension of the Anionic Surfactants in the Aqueous Solution and Role of Diffusion

The measurement and control of the dynamic surface tension (DST) for the surfactant containing solutions have a substantial role in many industrial and biological processes, e.g., agriculture (for easy spread of pesticides onto leaves), paint and coating industries, aerosol formation, as well as in biological processes, e.g., for effective functioning of the alveoli in the lung or in the analysis of human biological fluids, where a change in DST may be a diagnostic tool [53].

DST measurements were obtained using the bubble method. The changes in DST with time (life time of bubble) for different concentrations of ABS and ABSNa50 and such systems as water-AS; HCl–AS with and without heavy metal ions are presented in Figure 7. This Figure presents only the selected examples due to many data.

As presented in Figure 7 at higher surfactant concentrations, it is quicker to achieve equilibrium surface tension than at lower ones for all examined systems. The same relationship was observed for various surfactants [48,54–56]. In the water–AS systems, the DST is higher compared to that in the HCl–AS or HCl–AS–M(II) systems. As it was mentioned previously, the addition of HCl salts causes the changes in the system composition, and therefore the dynamic surface tension decreases. Due to the small difference in the structure of surfactants, the evolutions of DST changes with time look very similar for the same concentration of HCl and heavy metals (Figure 7e,f). When the HCl concentration increases (Figure 7i,j) despite the same surfactant and heavy metals, the plots mentioned above look different at the same surfactant concentration. With the HCl addition, the systems needed more time to reach equilibrium. Such behaviour is observed at higher surfactant concentrations. When the surfactant concentration is small, the changes are not so visible. At a large concentration of ABS or ABSNa50, more molecules of surfactants adsorb at the interface than at the small surfactant concentration, and the dynamic surface tension values are much lower. This behaviour was also observed previously in the earlier studies for the similar systems containing SDS [19] as well as by other researchers e.g., Qazi et al. [48] who studied the effect of high concentrations of NaCl on the surface tensions in equilibrium and dynamic stage of solutions containing the cationic (CTAB) or nonionic (Tween 80) surfactants or Le et al. (Aerosol-OT in 10 mM NaCl solution) [57]. The observed relationships indicate that there are differences only when the aqueous systems are compared with the other systems containing metal ions and acid. It should be assumed that, even if the surfactant forms ionic pairs in the presence of other ions, this does not affect the dynamics of the adsorption process significantly. The presence of such ion pairs and the resulting change in the surfactant nature should not significantly slow down adsorption largely. The decrease in CMC, as electrolytes are added to the aqueous surfactant solution, seems

to play an important role. A decrease in CMC means that the monomer concentration in the system is significantly reduced, which consequently slows down the adsorption process. In the systems under consideration the moving of micelles to the interface and then demicellation in the subsurface layer can be expected, which indicates that the kinetics of the adsorption will be affected by both micellar diffusion and monomer adsorption [58]. Moreover, with the addition of acid and metal ions in the systems under consideration, a large amount of micelles is present and it is expected that their diffusion to the interface will influence the adsorption kinetics to a large extent.
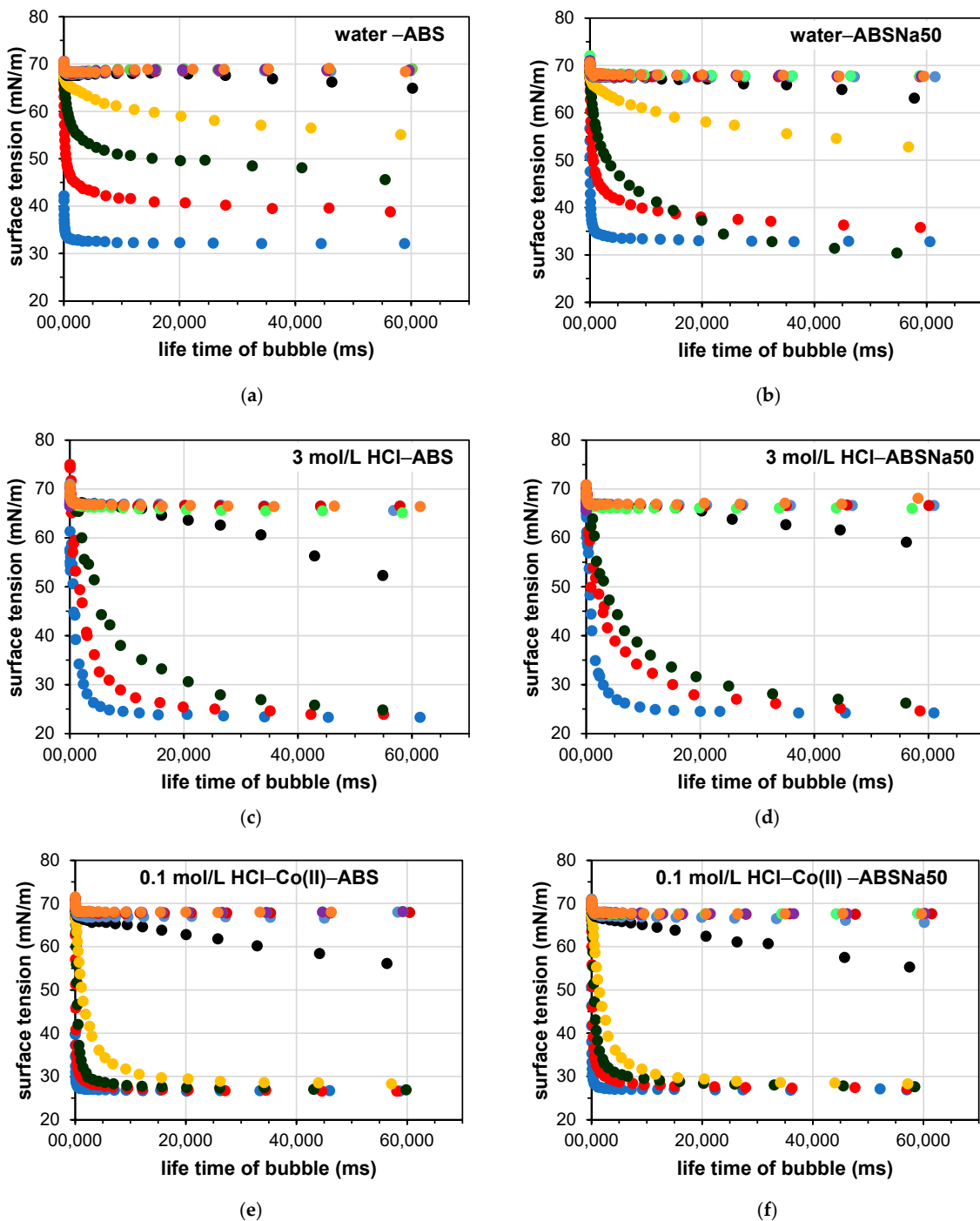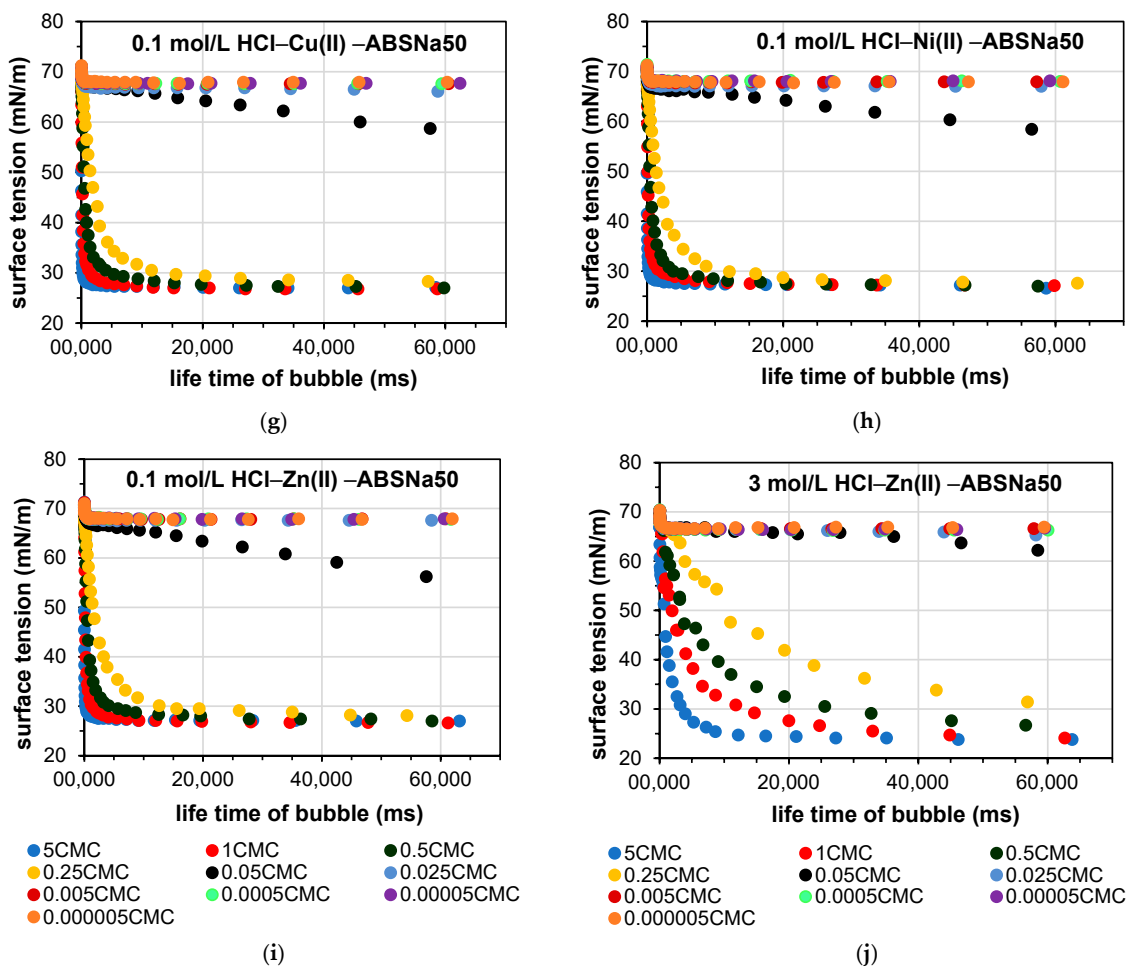
(a)

(b)

(c)

(d)

(e)

(f)

Figure 7. *Cont.*

(g)

(h)

(i)

(j)

Figure 7. Plot of DST versus time for different anionic surfactant concentrations (water-ABS (**a**), water-ABSNa50 (**b**), 3 mol/L HCl-ABS (**c**), 3 mol/L HCl-ABSNa50 (**d**), 0.1 mol/L HCl-Co(II)-ABS (**e**), 0.1 mol/L HCl-Co(II)-ABSNa50 (**f**), 0.1 mol/L HCl-Cu(II)-ABSNa50 (**g**), 0.1 mol/L HCl-Ni(II)-ABSNa50 (**h**), 0.1 mol/L HCl-Zn(II)-ABSNa50 (**i**), 3 mol/L HCl-Zn(II)-ABSNa50 (**j**)) measured by the maximum bubble pressure methods—the selected examples (5 CMC ABS = 0.0063 mol/L, 5 CMC ABSNa50 = 0.0073 mol/L).

The equations shown in Figure 8 are used to quantify the kinetic of adsorption.

$$D_{t \to 0} = \frac{1}{4} \times \frac{\pi \times a^2}{(RTc)^2} \tag{7}$$

$$D_{t \to \infty} = \frac{\pi}{4 \times \left(\frac{a \times c}{RT\Gamma^{S_z}}\right)^2} \tag{8}$$

$$\frac{\left[d\gamma/dt^{-1/2}\right]_{CMC}}{\left[d\gamma/dt^{-1}\right]_{c \,>\, CMC}} = \alpha \left(\frac{k_2 \times \pi}{4}\right)^{1/2} \tag{9}$$

The dynamic surface tension (N/m), D; approximation of short time, t→0 — **Equation (7)**

Plot: the dynamic surface tension (N/m) in the function of $t^{1/2}$ $(s^{1/2})$

α - the relative value of the monomer concentration in the solution with the concentration higher than CMC in relation to that equal to CMC

The dynamic surface tension (N/m), D; approximation of long time, t→∞ — **Equation (8)**

Plot: the dynamic surface tension (N/m) in the function of $t^{-1/2}$ $(s^{-1/2})$

R – the gas constant, T – the temperature, c – the concentration, Γ^{sz} - the surface excess at the interface.

The micelle dissociation rate constant, k_2

Plot: the dynamic surface tension (N/m) in the function of $t^{-1/2}$ $(s^{-1/2})$, the dynamic surface tension (N/m) in the function of t^{-1} (s^{-1}) — **Equation (9)**

$d\gamma/dt^{-1/2}$ - the derivative value approximated for a long time of dynamic surface tension, determined on the basis of the dependence of the surface tension versus the reversal square root from the life of the bubble, for t→∞ at c=CMC, $d\gamma/dt^{-1}$ - the derivative determined from the dependence of the surface tension on the inverse of the bubble life time for t→∞ at any concentration of c>CMC.

Figure 8. Characterization of the parameters used for diffusion determination in the ABS and ABSNa50 adsorption [59].

There are required three assumptions in order to obtain the linear short-time approximation relationship between γ(t) and $t^{1/2}$ and to fit the experimental DST data: (1) no back diffusion, (2) Henry's equation of state must be fulfilled, (3) the forward adsorption as a result of the spherical geometry is much smaller in comparison to the planar surface [53,60,61]. Equation (8) found applicability when $k_2\pi t \gg 1$, whereas the relative value of monomer concentration α is equal to 1 for the nonionic surfactants and less than 1 for the ionic surfactant (c > CMC) and α = 1 at c < 10 CMC. For c >> CMC α is stated as:

$$\alpha = \left[\frac{c}{cCMC}(1-\beta)\right]^{-\beta}$$ (10)

where β is the degree of counterions binding at the micelles.

Values of $D_{t\to0}$, $D_{t\to\infty}$ and k_2 for all considered systems (were obtained and are collected in Table 3, whereas the illustrations of the short- and long-time approximation for the HCl–AS–M(II) systems are presented in Figure 9. As follows from Figure 9 which presents the selected examples of surface tension (N/m) versus time ($t^{1/2}$ or $t^{-1/2}$), the obtained R^2 coefficients are high, therefore the diffusion coefficients were calculated. Due to the fact that D values are significantly dependent on the curve fitting, when the determination coefficients were low or very low the diffusion coefficients are not showed.

Table 3. Diffusion coefficients and micelle dissociation rate constant parameters obtained in the systems containing the AS surfactants (chosen examples).

	0.1 mol/L HCl–ABS–Co(II)			0.1 mol/L HCl–ABS–Cu(II)		
c (mol/L)	$D_{t \to 0}$ (m²/s)	$D_{t \to \infty}$ (m²/s)	k_2 (s⁻¹)	$D_{t \to 0}$ (m²/s)	$D_{t \to \infty}$ (m²/s)	k_2 (s⁻¹)
6.33×10^{-3}	5.33×10^{-12}	2.94×10^{-11}	35,200	4.10×10^{-12}	2.48×10^{-10}	64,640
1.27×10^{-3}	1.46×10^{-9}	2.68×10^{-11}	3930	1.55×10^{-9}	1.14×10^{-10}	5210
6.33×10^{-4}	4.33×10^{-10}	6.20×10^{-11}	62,900	6.32×10^{-10}	6.27×10^{-11}	93,272
3.17×10^{-4}	2.65×10^{-10}	2.08×10^{-11}	348,000	2.90×10^{-10}	5.59×10^{-11}	464,108
1.27×10^{-4}	6.17×10^{-10}	7.27×10^{-12}		6.11×10^{-10}	1.12×10^{-11}	
6.33×10^{-5}	2.93×10^{-9}	6.67×10^{-11}		2.53×10^{-9}	8.76×10^{-11}	
3.17×10^{-5}	1.16×10^{-8}	1.26×10^{-7}		9.34×10^{-9}	6.03×10^{-9}	
	0.1 mol/L HCl–ABS–Zn(II)			**0.1 mol/L HCl–ABS–Ni(II)**		
6.33×10^{-3}	5.35×10^{-12}	3.82×10^{-11}	35,355	5.35×10^{-12}	3.82×10^{-11}	35,355
1.27×10^{-3}	1.49×10^{-9}	2.20×10^{-11}	3802	1.49×10^{-9}	2.20×10^{-11}	3803
6.33×10^{-4}	5.51×10^{-9}	1.79×10^{-10}	3998	5.51×10^{-9}	1.79×10^{-10}	3999
3.17×10^{-4}	2.85×10^{-10}	1.71×10^{-11}	304,327	2.85×10^{-10}	1.71×10^{-11}	304,328
1.27×10^{-4}	4.95×10^{-10}	4.53×10^{-12}		4.95×10^{-10}	4.53×10^{-12}	
6.33×10^{-5}	2.55×10^{-9}	1.53×10^{-11}		2.55×10^{-9}	1.53×10^{-11}	
3.17×10^{-5}	1.05×10^{-8}	2.48×10^{-9}		1.05×10^{-8}	2.48×10^{-9}	
	0.1 mol/L HCl–ABSNa50–Co(II)			**0.1 mol/L HCl–ABSNa50–Cu(II)**		
7.31×10^{-3}	1.28×10^{-11}	2.78×10^{-10}	633	1.21×10^{-11}	1.24×10^{-11}	17,588
1.46×10^{-3}	5.30×10^{-10}	4.30×10^{-11}	525	5.49×10^{-10}	7.37×10^{-11}	12,475
7.31×10^{-4}	1.65×10^{-10}	3.64×10^{-11}	6662	1.79×10^{-10}	3.05×10^{-11}	158,102
3.66×10^{-4}	1.44×10^{-10}	5.21×10^{-11}	26,935	1.02×10^{-10}	3.49×10^{-11}	958,251
1.46×10^{-4}	5.17×10^{-10}	1.32×10^{-11}		4.52×10^{-10}	8.09×10^{-12}	
7.31×10^{-5}	2.05×10^{-9}	1.40×10^{-10}		2.31×10^{-9}	1.52×10^{-10}	
3.66×10^{-5}	7.07×10^{-9}	3.40×10^{-8}		8.65×10^{-9}	1.00×10^{-7}	
	0.1 mol/L HCl–ABSNa50–Zn(II)			**0.1 mol/L HCl–ABSNa50–Ni(II)**		
7.31×10^{-3}	1.11×10^{-11}	2.59×10^{-10}	20,290	1.08×10^{-11}	1.47×10^{-11}	23,628
1.46×10^{-3}	4.34×10^{-10}	2.68×10^{-10}	18,772	5.90×10^{-10}	1.75×10^{-10}	14,406
7.31×10^{-4}	1.55×10^{-10}	1.20×10^{-10}	209,952	1.75×10^{-10}	1.85×10^{-10}	184,938
3.66×10^{-4}	1.18×10^{-10}	1.08×10^{-10}	940,602	1.39×10^{-10}	1.52×10^{-10}	821,586
1.46×10^{-4}	4.70×10^{-10}	2.18×10^{-11}		4.02×10^{-10}	2.73×10^{-11}	1,653,535
7.31×10^{-5}	1.97×10^{-9}	2.88×10^{-10}		1.91×10^{-9}	6.15×10^{-10}	
3.66×10^{-5}	7.49×10^{-9}	3.69×10^{-4}		8.52×10^{-9}	1.11×10^{-5}	
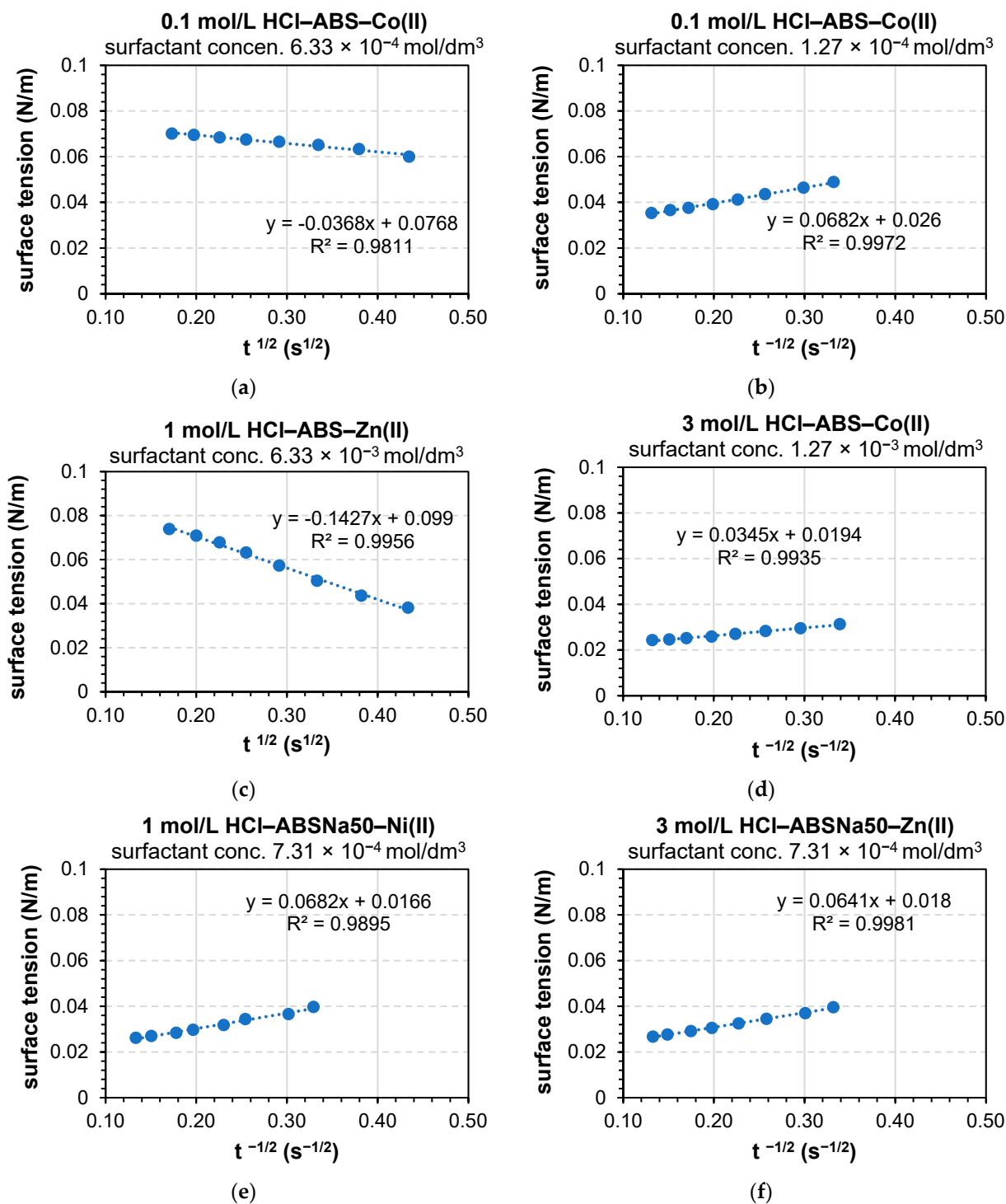
Figure 9. Selected examples of approximation plots (short, long time) in the HCl–AS–M(II) systems where AS indicates ABS (**a**–**d**) and ABSNa50 (**e**,**f**) surfactants.

As it was observed based on the diffusion coefficients, the values collected in Table 3 increase with the increasing surfactant concentration. The same relationship was observed for the other surfactants, for example, dodecyltrimethylammonium bromide [61]. When the concentration of surfactant is small, the greater mobility of molecules is observed. At the same time, at higher surfactant concentrations, the diffusion coefficients are smaller, indicating smaller surfactant particles mobility. Such observations indicate that diffusion plays a role in the surfactant adsorption. The results indicate that adsorption is significantly influenced by the surfactant monomer concentration, while the formation of micelles has

no effect on the kinetics of adsorption. Such observation is in agreement with the Ward and Tordai's theory, according to which the characteristic adsorption time correlates only with the monomer concentration. On the other hand, it is assumed that at the concentrations above CMC, the adsorption mechanism changes from the diffusion-controlled to the adsorption barrier-controlled one or mechanism based on the mixed diffusion–adsorption barrier [58,62].

The values of derivatives $d\gamma/dt^{-1}$ and $d\gamma/dt^{-1/2}$ were applied also for calculations of the k_2 constant. As it was pointed out the significant changes in the surfactant concentration by an order of magnitude, e.g., from 10^{-3} to 10^{-4} (concentration decrease) cause an increase of k_2, whereas at the value 10^{-3} Fainerman and Makievski [63] also measured the DST of the sodium tetradecylsulphate, sodium bexadecylsulphate solutions and Triton X-100 in water to obtain the constant micelle dissociation rate and observed that this parameter has higher value when the higher surfactant concentration is considered, particularly for ionic surface activity compounds (for c > 10–30 CMC). This phenomenon can be described by a transition of the micelle shape and a strengthening of the intermolecular repulsion in the system. Moreover, the k_2 parameter increases with increasing temperature for the ionic surfactant as a consequence of the nature of molecular interactions in the case of ionic and nonionic surfactants.

4. Conclusions

The surface properties and the adsorption parameters of the anionic surfactant dodecylbenzene sulfonic acid (ABS) with the heavy metal ions and hydrochloric acid containing systems were presented and compared with the results for sodium dodecylbenzene sulfonate (ABSNa50). The critical micelle concentrations (CMC) obtained based on the adsorption isotherms were the highest in the water containing system being 2.33 mmol/L and 1.52 mmol/L, for ABS and ABSNa50, respectively. The adsorption of ABS and ABSNa50 at the interface and the dramatic decrease of ɣwith the decrease in the surfactant concentration were observed. The aggregation behaviour of the ABS in water could be explained by the dimer mechanism involving hydrogen bonds. The addition of both HCl and heavy metal ions changed the CMC by a shift toward lower concentrations with the increasing HCl concentration for both surfactants. It was observed that varying the concentration of hydrochloric acid had a more significant effect on the CMC values obtained in relation to different metal ions at constant concentration. The obtained values indicate that the adsorption of ABS and ABSNa50 surfactants at the air/water interface is spontaneous and controlled by diffusion.

In conclusion, the presented analyses of the behaviour of the anionic surfactants in the system containing heavy metal ions and HCl acid are very significant from a practical point of view. Based on them, it is possible to design systems in which micelles will be characterized by specific stability controlling the surfactant structure, its concentration or physicochemical conditions (e.g., presence of electrolyte, temperature, and pressure) enabling for technological processes as well as design control. Further research in this area, in particular on the behaviour of surfactants at different metal ion concentrations, should be continued.

Author Contributions: Conceptualization, A.W., K.S. and Z.H.; methodology, A.W. and K.S.; validation, A.W.; formal analysis, A.W.; investigation, A.W.; writing—original draft preparation, A.W. and K.S.; writing—review and editing, A.W., K.S. and Z.H.; visualization, A.W.; supervision, A.W.; project administration, A.W.; funding acquisition, A.W. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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