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Adsorption effectiveness and adsorption efficiency of chosen surfactants

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1. INTRODUCTION

The world around us consists of chemical and physical interactions, as well of those processes happening between the surfaces. It is always a challenge to describe what mechanisms dictate the conditions and which actually appear in such areas. These informations are not only valuable because of their industrial applications, but also from scientific point of view. Interfaces and surfaces are in great favour of various substances called surfactants. Those amphiphilic structures (as they consist of hydrophilic and hydrophobic part, thus called amphiphilic) can adsorb at interfaces in oriented way [1–5].

The adsorption of those substances gives insight of the phenomena existing, which allows to describe properties of such interfaces and mechanisms dominating them. It is very useful in determining surfaces hydrophobicity or hydrophilicity, surfactants concentration at the interface, its packing and coverage, but also surface wettability and basic thermodynamic characteristic like enthalpy or entropy.

Keeping in mind thermodynamic properties, surfaces can be characterised by effectiveness (surfactant concentration that is required for inducing a specific effect) and efficiency (maximum effect that can be induced by a surfactant at the interface) [1]. They may seem as twins, but in fact, they run in opposite ways most of the time. It is caused by the fact that effectiveness bases more on interface saturation with surfactant orientation and functional groups of the compound, whereas efficiency bases solely on the functional groups.

2. SOLID-LIQUID INTERFACE

Adsorption at such interface is dictated by a few factors. The most important are, in fact, the structural groups gathered on the surface of solid body as well as their nature – whether they are highly nonpolar or highly charged. Then, the structure of surfactant itself is very important – whether it is non-ionic or ionic or if the hydrophobic chain is branched, long or short, or even aromatic. The last important factor is the aqueous phase – the pH value, content of the electrolytes as well as the number of additives such as alcohols or urea and the temperature. Factors like these allow to determine adsorption mechanisms as well as its efficiency and effectiveness. When it comes to adsorption mechanisms there are a few main ones:

- ion exchange,
- ion pairing,
- acid-base interactions,
- polarization of π electrons,
- dispersion forces,
- hydrophobic bonding.

Ion exchange allows to replace ions adsorbed on the substrate by surfactant ions from the solution. Ion pairing depends on oppositely charged sites which are unoccupied and surfactants adsorbing onto them. Acid-base interactions connect to Lewis acid-base reactions. Polarization of π electrons takes place when adsorbent has positively charged sites and adsorbate stands out with its aromatic nuclei rich in electrons. Adsorption with use of dispersion forces appears when dispersion forces of London-van der Waals happen between adsorbate molecules and the adsorbent. Adsorption by hydrophobic bonding occurs thanks to tendency of hydrophobic groups to escape from aqueous solutions and adsorb by aggregating their chains onto solid adsorbent [1].

When surfactant molecule orients itself with its hydrophilic groups away from solid substrate it will make the surface more hydrophilic; when surfactant molecule orients itself with its hydrophobic groups away from the surface, the surface becomes more hydrophobic. To see what the predominant orientation is, one can use measurements of contact angle on nonporous smooth plates. The higher values of contact angle, the greater hydrophobicity of the solid. Moreover, if the solid body can be finely divided into particles, the surfactant adsorption may make it more hydrophilic and it will disperse more easily in the water. If it will make it more hydrophobic, then particles will most likely float or settle out. In principle, more hydrophobic particles will disperse easier in nonpolar phases and more hydrophilic particles will disperse easier in polar solvents.

When observing interfaces, such as solid-liquid ones, there's needed a determination of few factors that will shed some light on the adsorption itself. Firstly, one must determine what is the amount of adsorbed surfactant per unit area or unit mass of the solid adsorbent – the surfactant concentration which hints how much of the adsorbent (or more precisely adsorbent surface) has been covered. Next, the efficiency of surfactant adsorption. It connects to the surfactant equilibrium concentration in the liquid phase which is needed to get a given surface concentration. The effectiveness of adsorption connected to surface saturation is also required. Moreover, one of the most important factors is surfactant orientation and finally, properties of the adsorbent itself. All the mentioned above variables influence adsorption isotherm. Adsorption isotherm is expression of mathematical nature and relates the adsorbate concentration at given interface to liquid phase equilibrium concentration. It's the usual method of showing adsorption at the liquid-solid interfaces.

The Langmuir Adsorption Isotherm is expressed by the equation [1, 6]:

$$\Gamma_1 = \frac{\Gamma_m C_1}{C_1 + a} \tag{1}$$

Where Γ_m is surfactant surface concentration in mol/cm^2.

C_1 is the surfactant concentration in the liquid phase when adsorption is at its equilibrium; a is a constant [= 55.3 exp($\Delta G^{o}/RT$)] expressed in mol/dm^3 and ΔG^{o} is adsorption free energy.

Langmuir Adsorption Isotherm can be observed in surfactant solutions. There are a few conditions that have to be met to observe Langmuir adsorption: a) homogenous adsorbent, b) equal molar areas of the surface for both solvent and substrate, c) ideal behaviours of both solvent and substrate which means that there is no substrate-substrate, solvent-substrate or solvent-solvent interactions, d) the film produced through the adsorption is monomolecular [7]. If adsorption fulfils Langmuir equation, the values of a and allow to calculate (when surface saturation is present) area of molecules adsorbed as well as adsorption free energy present when solvent it infinitely diluted. To see if the adsorption follows Langmuir equation, one needs its linear form.

$$\frac{1}{\Gamma_1} = \frac{a}{\Gamma_m C_1} + \frac{1}{\Gamma_m} \tag{2}$$

The relation C_1/Γ_1 should appear as straight line of slope can be expressed as $1/\Gamma_m$.

Even if data obtained fits the equation concluded by Langmuir, it does not mean that the model assumptions listed above are completely met. In most cases, there is mutual compensation of factors that may influence Langmuir isotherm and its shape. This is the case for many surfactants. The factors that may affect the isotherm shape are as follows [8]:

1. Surfactant micellization which flattens the curve of the isotherm and causes insignificant activity decrease with simultaneous increase of surfactant concentration in liquid phase.
2. Potential of the surface will reduce adsorption if it has the same sign as the ion of surfactant molecule. Therefore, it reduces isotherm's slope. In reverse situation (when surface sign is opposite to the sign of surfactant ion) it increases the slope of isotherm.
3. Solid adsorbent heterogeneity which causes Langmuir isotherms to resemble BET or Freundlich one. When adsorbent has high-energy sites, the isotherm has higher

slope than it should have. If it has low energy sites, isotherm slope is also low.

4. Lateral interactions are attractive interactions that can affect isotherm by making it steeper, stepped or S-shaped.

Mechanism of adsorption has been proposed by Gu and Zhu [9–11]. This two-step adsorption mechanism begins with adsorption of surfactant molecules individually as molecules or ions. Then, as surface aggregates form, there's an increase of adsorption. Surface aggregates are formed because of presence of hydrophobic chains which interact with each other. To describe such adsorption, the following equation has been suggested:

$$\Gamma_1 = \frac{\Gamma_\infty K C_1^n}{1 + C_1^n} \tag{3}$$

Γ_∞ is limiting adsorption of surfactant when concentration C_1 is high, K is equilibrium constant during the process of surface aggregation, n is number of aggregates at the surface in general isotherm of adsorption.

Solutes that are poorly purified on impure or heterogeneous adsorbents pass through maximum on adsorption isotherms. Such phenomena are very possible if one deals with gas phase or adsorption present in concentrated solutions. The theoretical grounds of this event are hard to explain in dilute surfactant solutions. Absence of such phenomena is observed after adsorbent and solute purification as they may connect to the impurities.

3. LIQUID-GAS AND LIQUID-LIQUID INTERFACES

When it comes to liquid-gas or liquid-liquid interfaces, determining how much of surfactant has been adsorbed is often not considered. The problem lies in difficulty of pointing the interfacial region and isolating it from the bulk phases. Instead, one can determine such parameter indirectly by applying interfacial or surface tension measurements. Relation of surface (interfacial) tension and concentration of surfactant is used to describe surfactant adsorption rather than isotherms of adsorption.

To determine adsorbed amount of surfactant per interface unit area one can use Gibbs equation which describes adsorption in such cases.

The Gibbs equation has the following form [12]:

$$d\gamma = -\sum_i \Gamma_i d\mu_i \qquad (4)$$

$d\gamma$ – describes the interfacial or surface tension change present in the solvent,
Γ_i – describes any component of surface excess concentration,
$d\mu_i$ – describes change in the chemical potential.

For non-ionic surfactants Gibbs equation has the following form:

$$d\gamma = -RT\Gamma_i dlnC_1 = -2.303RT\Gamma_i dlogC_1 \qquad (5)$$

Gibbs equation is fundamental for processes of adsorption where monolayers are formed. Surface excess can be defined as the amount of adsorbate per unit area which is transferred from bulk phase beyond range of adsorption forces during process of adsorption to interfacial phase within range of adsorption forces. If solutes are surface active, the surface excess Γ_i is almost equal to present concentration of the surface without significant error. By using appropriate Gibbs equation, one can easily calculate concentration of a surfactant at the given interface [1, 26].

The area occupied by the surfactant molecule can provide hints about the packing and surfactant orientation at the interface. There is a possibility to compare this information with molecular models. Typical relation between values $\gamma -$ log and concentration C_1 form a plot which allows to determine critical micelle concentration (CMC). CMC value can be obtained in the breaking point of the curve. CMC can be determined as such concentration of a surfactant where micelles start to form and addition of surfactant molecules (monomers) doesn't change the concentration of monomeric form in the solution. Surface tension of such solution remains almost constant, because only monomeric form increase could be contributing to its reduction. Near the CMC, the slope of the curve is basically constant and surface concentration has a constant maximum value. Van Voorst Vader concluded that interface is saturated by the time CMC is obtained [13]. The reduction of surface tension is caused mainly by the increasing activity of substrate (surfactant) in the bulk phase in comparison to interface.

4. ADSORPTION EFFECTIVENESS AT LIQUID-LIQUID AND LIQUID-GAS INTERFACES

When surface achieves saturation expressed as Γ_m, surface excess concentration can be used for measurements of adsorption effectiveness at liquid-liquid or liquid-gas interfaces. Surface excess concentration is the maximum of the adsorption. Adsorption effectiveness is important for describing and understanding properties such as wetting, foaming, and emulsification which are characteristic for each surfactant. Interfacial films that are coherent have different properties at the interface than noncoherent, loosely packed films. Hydrophobic chains adsorbed at liquid-gas or simply hydrocarbon aqueous solutions interfaces are not very close-packed in contrast to interface at saturation adsorption. If the surfactant has a single group that is hydrophilic, no matter if ionic or non-ionic, the area occupied by such molecule is determined by the hydratable hydrophilic group. If second hydrophilic group is present in the surfactant molecule, the part of molecule that exists between hydrophilic groups will lie flat. The area occupied by the molecule at interface significantly increases [1].

4.1. Langmuir, Szyszkowski, and Frumkin equations

Langmuir equation has the following form [8]:

$$\Gamma_1 = \frac{\Gamma_m C_1}{C_1 + a} \tag{6}$$

and relates surface excess concentrations with their bulk counterparts.

Szyszkowski equation has the following form [1, 14]:

$$\gamma_0 - \gamma = \pi = 2.303RT\Gamma_m \log\left(\frac{C_1}{a} + 1\right) \tag{7}$$

where γ_0 is solvent surface tension and π is pressure of the surface (how much surface tension is reduced). Szyszkowski equation relates bulk concentrations and surface tensions.

Frumkin equation has the following form [15]:

$$\gamma_0 - \gamma = \pi = 2.303RT\Gamma_m \log\left(1 - \frac{\Gamma_1}{\Gamma_m}\right) \qquad (8)$$

and relates surface concentration (excess) with surface tensions.

All these equations can be obtained from surface equation of state proposed by Lucassen-Reynders if ideal behaviour is assumed (coefficients are close to unity). It is possible to do that with ionic surfactants at hydrocarbon aqueous solutions and solution-air interfaces [16].

4.2. Adsorption efficiency at liquid-liquid and liquid-gas interfaces

If one wants to compare surfactants performance at liquid-liquid and liquid-gas interfaces, there's need of introducing parameter that will define surfactant concentration required to produce a certain amount of adsorption process in the liquid phase. It is possible to call it the efficiency of surfactant adsorption if there's a way to relate it to the free energy change.

To measure efficiency in a convenient way, one can use the negative logarithm of surfactant concentration in the bulk phase which allows to produce a 20 mN/m surface or interfacial tension reduction of the solvent, i.e. $-logC_{(-\Delta y=20)} \equiv pC_{20}$.

Assumptions must be considered [1]:

1. Ideal situation in case of adsorption efficiency is a function of surfactant minimum concentration in the bulk phase which allows to produce maximum adsorption (saturation).
2. It requires a complete $\gamma - logC_1$ plot, but literature allows to narrow it down, because pure solvent surface tension decreases to about 20 mN/m. Surfactant adsorbs and surface excess concentration Γ_1 value is close to the value of saturation.

Basing on these assumptions, surfactant concentration in bulk liquid phase needed to reduce surface (interfacial) tension by 20 mN/m will be a good way to measure efficiency of surfactant adsorption. It is close enough to minimum concentration required to obtain saturation adsorption at examined interface pC_{20}, negative logarithm of the concentration of the bulk phase is used more often than C_{20} concentration, because it can be easily related to the standard free energy change ΔG^{o}. ΔG^{o} represents transfer of surface-active substrate from bulk phase (its interior part) to the interface.

The advantage of relation with standard free energy is that its total change can be divided into individual structural groupings and their standard free energies. It allows to make correlations between surfactant interfacial properties and functional groups as well as structural groupings in the molecule. By using Langmuir (Eq. 6) [8] and Szyszkowski (Eq.7) [1, 14] equations, it is possible to see that relation of efficiency factor pC20 and number of carbons present in hydrophobic group (in the straight chain) is linear and increases with the increase of carbon atoms in the molecule. If the value of pC_{20} increases, the surfactant adsorbs more efficiently and reduces surface interfacial tension more efficiently as well. In other words, one needs smaller concentrations in the bulk liquid phase to achieve saturation adsorption and reduce interfacial/surface tension by 20 mN/m.

Adsorption efficiency increases steadily when length of the hydrophobic group increases up to 20 carbons. It's different for adsorption effectiveness, which decreases when hydrophobic group length gets beyond 16 carbon atoms [1].

To summarise, adsorption efficiency expressed by pC_{20} value can be increased by following factors [1]:

1. Hydrophobic chain length and number of carbons.
2. Hydrophobic chain should be rather straight than branched. Straight chain with the same number of carbons as branched chain will increase adsorption efficiency more effectively.
3. Single group of hydrophilic properties at the end of the chain. It will be more effective than group placed in central position.
4. Non-ionic and zwitterionic groups of hydrophilic properties.
5. To decrease effective charge in hydrophilic group one should use less hydrated counterion or change (increase) of the ionic strength.

5. COMPARISON OF ADSORPTION EFFECTIVENESS AND EFFICIENCY OF CHOSEN SURFACTANTS AT THE WATER-AIR INTERFACE

Gibbs standard free energy explains the processes accompanying transfer of substrate (in this case surfactant molecules) to surface layer of liquid-air interface from the bulk phase. It is important to determine whether process goes spontaneously or if it is not spontaneous at all. The denser packing of the surfactant at the interface, the better reduction of surface tension. For many surfactants, the minimal value is obtained around CMC, but maximum value of Gibbs surface excess concentration (also called saturated monolayer) may appear in concentration lower than CMC. When saturated monolayer is forming, surface tension decreases significantly from the start of its formation to the value of CMC [17]. When it comes to surface active ions, changes in standard Gibbs free energy are caused by transfer of hydrophobic parts of the molecule from water to air phase and simultaneous change of hydration degree of hydrophilic part. At the same time, micellization energy connects to standard Gibbs free energy and interaction of surface-active molecule or ion with the water phase. To determine aggregation and adsorption activity of active ions, it is important to consider their contactable area.

Surfactants are various types of chemical compounds that are present in almost every aspect of our life. They are widely used in food industry, pharmaceutics, cosmetics and even in confectionery. The universality of surface-active agents comes from their specific, amphiphilic build: they consist of hydrophobic chain called “tail” with affinity to nonpolar compounds, e.g. lipids, and hydrophilic “head” with affinity to polar compounds, e.g. water. Unfortunately, huge use of surfactants makes them accumulate in the environment, especially in ground waters. Surfactants damage flora and fauna and can cause severe allergies. In that case, many companies decide to limit their surfactant usage and reach for substances present in nature which have very similar, if not better, properties. Most of those compounds are produced by microorganisms and are called biosurfactants.

Many papers related to different properties (CMC, aggregation number, surface excess concentration) of various types of surfactants can be found in the literature. However, it is difficult to find papers describing the same properties for different surfactants. It seems interesting to compare adsorption effectiveness and efficiency of chosen surfactants at the water-air interface which decide about practical surfactants application. For this consideration anionic: sodium dodecylsulfate (SDDS), cationic: cetyltrimetylammonium bromide (CTAB), nonionic: Triton X-100 (TX-100) and biosurfactants: surfactin (SF) and monorhamnolipid (RL) were chosen. These compounds were selected for their interesting practical properties and wide application in many industrial branches and everyday life.

SDDS is one of the most well-known surfactants and one of the most extensively investigated. It is used in laundry detergents and cleaners. It has a wide application in removal of oil residues [18]. CTAB is a common substance used in synthesis of nanoparticles and reduction of PAHs (polycyclic aromatic hydrocarbons) bioavailability. It has application in production of hair conditioners [19]. TX-100 is widely used in bioremediation, especially when it comes to hydrophobic hydrocarbons contaminations. It is used in metal cleaners, detergents, pesticides and textile industry [20]. Rhamnolipid and surfactin both have antitumor and antiviral properties, can interact as antibiotics, enzyme and toxins inhibitors, and they are widely investigated as alternatives for classical surfactants. They are also investigated as surgical devices protectors [21].

It is obvious that studied surfactants are characterized by different properties, also by adsorption efficiency at the water-air interface which is correlated with pC_{20}. To evaluate this parameter the data of surface tension of aqueous solutions of studied surfactants was taken from literature (Fig. 1) [17, 22-24].

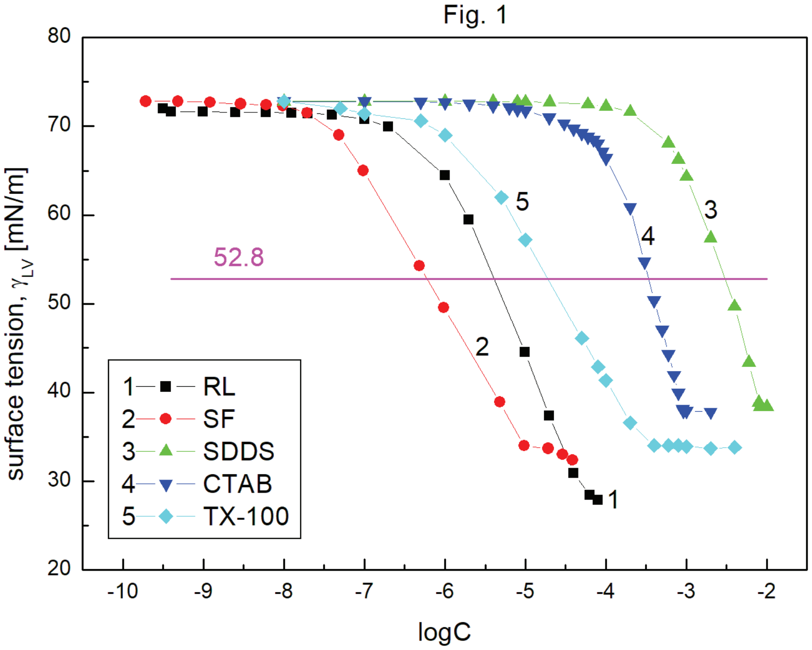

Fig. 1. A plot of surface tension (γ_{LV}) of aqueous solutions of surfactants vs. the logarithm of their concentration (logC). Curves 1-5 correspond to

rhamnolipid (RL), surfactin (SF), sodium dodecylsulfate (SDDS), cetyltrimetylammonium bromide (CTAB) and Triton X-100 (TX-100), respectively.

Unexpectedly, the largest value of this parameter among the described compounds possesses a biosurfactant, namely surfactin (6.22) (Fig.2).

Fig.2.

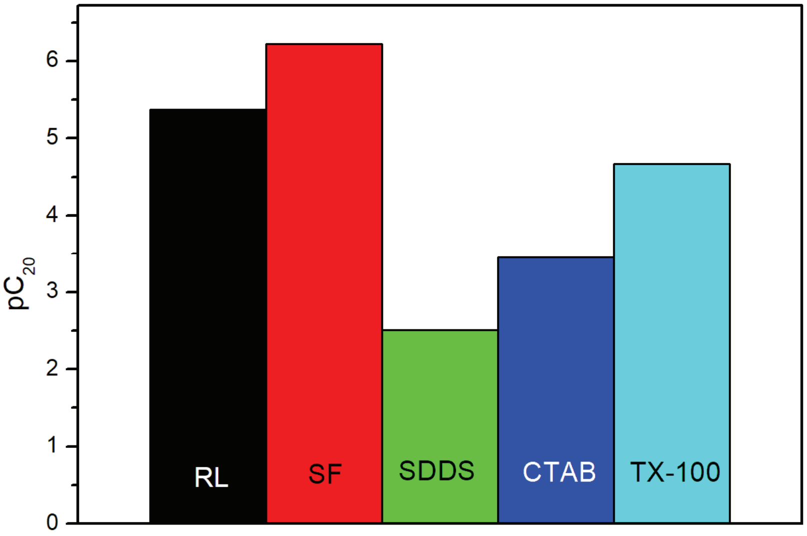

Fig. 2. The values of pC_{20} parameter for rhamnolipid (RL), surfactin (SF), sodium dodecylsulfate (SDDS), cetyltrimetylammonium bromide (CTAB) and Triton X-100 (TX-100), respectively [17, 22-24].

From Fig. 2, it results that between classical surfactants efficiency, the non-ionic TX-100 adsorption is higher than that of ionic CTAB and SDDS. SDDS, which is one of the most commonly used surfactants, has the lowest value of pC_{20} (2.51). According to the obtained data, SF is the most efficient surfactant and its lowest concentration is needed to reduce the surface tension of water by 20 mN/m. Also, in the case of SF, the saturated adsorption monolayer at the water-air is formed at the lowest concentration. The question arises: is the highest value of maximal surface excess concentration observed also in the case of surfactin? To answer that question, one must analyse literature data connected to this concentration. It should be remembered that maximal Gibbs surface excess concentration was determined based on straight linear part of relationship between the logarithm of surfactant concentration and the surface tension of surfactant aqueous solution.

The values of maximal Gibbs surface excess concentration (Γ_{max}) of chosen surfactants were taken from the literature [23–25] and presented in Table 1 together with corresponding surface areas occupied by surfactant molecules at the water-air interface (A).

These surface areas were calculated from the following equation:

$$A = \frac{1}{N\Gamma_{max}} \tag{9}$$

where N is the Avogadro number.

Table 1. The values of maximal Gibbs surface excess concentrations and corresponding surface areas occupied by surfactants at the water-air interface.

Surfactant	Γ_{max} [mol/m^2]	A [Å^2]
RL	2.01×10^{-6}	82.60
SF	1.38×10^{-6}	120.31
CTAB	3.10×10^{-6}	53.57
SDDS	3.20×10^{-6}	51.88
TX-100	2.83×10^{-6}	58.67

From Table 1 it results that the values of Γ_{max} and A for classical non-ionic and ionic surfactants differ from each other quite significantly. Ionic surfactants show better adsorption at the water-air interface. It also appeared that the highest value of maximal Gibbs surface concentration is observed in the case of anionic SDDS. This value is reflected in the smallest surface area occupied by this surfactant at the water-air interface. In the case of surfactin, in contrary to its efficiency, the lowest value of Γ_{max} and highest A are observed. Of course, one must remember that surface area occupied by surfactant molecule depends on its structure and presence of different kind of functional groups. The physicochemical values presented in Table 1 indicate that effectiveness of adsorption of SDDS at the water-air interface is the highest while adsorption effectiveness of SF the lowest.

Summarizing, it can be stated that high efficiency does not have to be accompanied by high effectiveness and vice versa. If we want to choose a surfactant for the given practical applications, we must take various properties into account.

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