Fluoro- vs hydrocarbon surfactants: Why do they differ in wetting performance?

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ABSTRACT

Fluorosurfactants are the most effective compounds to lower the surface tension of aqueous solutions, but their wetting properties as related to low energy hydrocarbon solids are inferior to hydrocarbon trisiloxane surfactants, although the latter demonstrate higher surface tension in aqueous solutions. To explain this inconsistency available data on the adsorption of fluorosurfactants on liquid/vapour, solid/liquid and solid/vapour interfaces are discussed in comparison to those of hydrocarbon surfactants. The low free energy of adsorption of fluorosurfactants on hydrocarbon solid/water interface should be of a substantial importance for their wetting properties.

Contents

1. Introduction

Fluorosurfactants are chemical compounds composed of two parts: polar hydrophilic head and highly hydrophobic fluorocarbon tail. Fluorocarbons have outstanding physico-chemical properties determined by the very special properties of fluorine. The specific properties of fluorocarbon chains (F-chains) as compared to hydrocarbon ones (H-chains) are discussed in detail in [1–3] and can be summarised as follows.

Fluorine has a larger size than hydrogen, it is more electronegative, but have smaller polarizability and high ionization potential. As a consequence fluorocarbon chains are more bulky than those of

hydrocarbons: according to [3] the mean volumes of CF_2 and CF_3 groups can be estimated as 38 A^3 and 92 A^3, whereas those of CH_2 and CH_3 are around 27 A^3 and 54 A^3, respectively. Cross section of F-chains is in the range of 27–30 A^2, whereas that of H-chains in the range of 18–21 A^2 [3]. F-chains are more rigid and often have helical conformation.

The C−F bond is very strong and chemically stable, actually being the most stable single bond in organic chemistry [1,2] determining the high chemical and thermal stability of fluorocarbons.

Because of low polarizability of fluorine the van der Waals interactions between fluorinated chains are weak, resulting in low cohesive energy of fluorocarbons and as a consequence low dielectric constant, high vapour pressure, high compressibility, high gas solubility, low surface tension, high surface activity in aqueous solutions and low critical micelle

concentration (CMC) [1–3]. The hydrophobicity of fluorocarbon chains is so high that they have a unique property being both hydrophobic and oleophobic, i.e. they are surface active not only in aqueous, but also in hydrocarbon solutions. The surface activity of fluorocompounds dissolved in organic liquids is discussed in detail in [1].

Owing to their outstanding properties and despite their high costs fluorocarbons extend progressively their fields of applications during several last decades [1]. Very promising are biomedical applications, for example emulsions of fluorocarbons in water are considered as a tool for oxygen delivering to the tissues [1–4] due to their high biocompatibility and non-toxicity. Although biomedical and pharmacological applications of fluorosurfactants are restricted by their toxicity [5,6], according to [2] the replacement in a surfactant of hydrocarbon chain by a fluorocarbon one usually does not result in the increase of toxicity, rather opposite. Introducing of fluorocarbon chain in a surfactant reduces also its haemolytic activity [2]. Thus, taking into account much higher surface activity and therefore smaller concentrations required, replacement of hydrocarbon surfactant by the fluorocarbone ones can be considered as preferable from the biomedical point of view and indeed, during the last decade fluorocarbon surfactants extend their biomedical applications, in particular in drug and gene delivery systems [7].

Many other important applications of fluorosurfactants such as levelling off paints, coatings, including stain-resistant coatings for clothing fabrics, leather, upholstery, and carpets, floor polishers, adhesives, anti-fogging and anti-static agents, cleaners, fire fighting foams and powders, flotation, crystal growth etc. are discussed in [1]. Ones of the very new applications are self-cleaning oleophobic surfaces [8] and solar cells [9,10]. The importance of fluorosurfactants is confirmed also by the fact that many new products with improved properties and biocompatibility appeared during last years [10–14].

Many applications of fluorosurfactants are based on their wetting and spreading properties. An example is the aqueous film-forming foams, AFFF, used to extinguish fires in liquid fuels and solvents. The essential feature of AFFF is the possibility to spread aqueous film on the surface of liquid hydrocarbon and in this way to prevent the access of oxygen to fire and also to reduce the evaporation of hydrocarbon [1, 15,16]. Therefore it is obvious that the spreading properties of foam forming liquid are of great importance for this application. To ensure the quick and complete spreading, the foaming liquid contains both hydrocarbon and fluorocarbon surfactants: the hydrocarbon surfactants decrease the hydrocarbon/water interfacial tension, whereas fluorocarbon surfactants lower water/air surface tension to values smaller than hydrocarbon surfactants can do creating in such a way a positive spreading coefficient of aqueous solution on hydrocarbon liquid [15]. Good wetting properties are also crucial for applications in paints and coatings [1].

At the same time it is well known that the aqueous solutions of fluorosurfactants do not wet such commonly used hydrophobic surfaces as polyethylene and polypropylene, although those surfaces are completely wetted by solutions of hydrocarbon trisiloxane surfactants having higher surface tension [17]. The trisiloxane surfactants were even referred to as "superspreaders" due to their outstanding wetting properties [18–20]. The contact angles of the solutions of fluorocarbon surfactants on hydrocarbon solids are higher than expected [1,21].

The aim of this review is to discuss why the wetting properties of the aqueous solutions of fluorocarbon surfactants on hydrocarbon solids are worse than those of hydrocarbon surfactants by comparing the available data on the adsorption of fluorosurfactants and hydrocarbon surfactants on liquid/vapour, solid/liquid and solid/vapour interfaces and to identify the ways to improve their wetting characteristics.

The paper is organised as follows: in the next section the wetting phenomena will be discussed with emphasis on the surfactant solutions following by some examples on the spreading performance of fluorosurfactant solutions on hydrocarbon substrates as compared with hydrocarbon surfactants; then the surface properties of fluorocarbon

surfactants will be considered on liquid/vapour, solid/liquid and solid/vapour interfaces. Finally the concluding remarks outlining the possible future work are presented.

2. Wetting of hydrophobic surfaces by surfactant solutions

Spreading of liquid over the surface of other liquid or solid is often an essential part of a number of processes, for example, painting and coating, fire extinguishing film-forming foams, herbicide application in agriculture, lung surfactant replacement therapy, etc. On the macroscopic level wetting equilibrium of a liquid droplet on a solid substrate is described by the Young equation:

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos\theta \qquad (1)$$

where (see Fig. 1) σ_{sv}, σ_{sl}, and σ_{lv} are the solid/vapour, solid/liquid and liquid/vapour surface tensions respectively, and θ is the contact angle. For the comprehensive discussion on applicability Eq. (1) and appropriate values of the contact angle see [22,24]. Eq. (1) is valid only for the flat, rigid, smooth and essentially homogeneous solid surface and the value of the static advancing contact angle is the best approximation for θ [22]. The corresponding contact angles on rough and heterogeneous surfaces are described by Wenzel and Cassie–Baxter equations, respectively [23]. These angles differ from θ predicted according to Eq. (1) [22]. Eq. (1) is only a macroscopic approach, which does not take into account the complicated shape of the liquid profile near the three phase contact line [24]. Nevertheless, Eq. (1) provides a good first approximation and is frequently used.

The work of spreading, also known as the spreading coefficient [21,25]

$$W_s = S = \sigma_{sv} - (\sigma_{sl} + \sigma_{lv}) \qquad (2)$$

is used below. Liquid spreads over a solid substrate if $S > 0$. The same criterion is used also for spreading on a liquid surface [26].

It follows from Eq. (1) that $cos(\theta) > 0$, i.e. $\theta < 90°$, only if $\sigma_{sl} < \sigma_{sv}$. On the other hand according to Eq. (2) the complete wetting is only possible if $\sigma_{lv} + \sigma_{sl} \leq \sigma_{sv}$, i.e. the only way to attain the complete wetting with an initially non-wetting liquid is to decrease one of or both σ_{sl} and σ_{lv} provided that σ_{sv} remains constant. It is well known that adsorption of surfactants on solid/liquid or liquid/air interfaces decreases corresponding interfacial tensions. This is the reason why surfactant solutions can wet hydrophobic surfaces non-wetted by pure water.

For surfactant solutions the adsorption of surfactants change all three surface energies σ_{sl}, σ_{sv} and σ_{lv} and they can differ substantially from the corresponding values for pure water [22,24]. This is the most probable reason of absence of a direct correlation between the surface tension of aqueous solution and its wetting properties. To understand the wetting properties of surfactant solutions, adsorption on both liquid/air and solid/liquid interface should be taken into consideration. Below we consider how the presence of surfactant and in particular fluorosurfactant affects each term included in the spreading coefficient S.
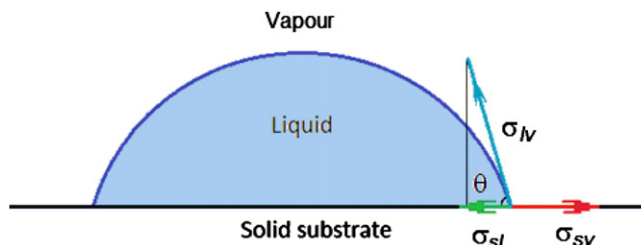

Fig. 1. Droplet of a partially wetting liquid on a solid substrate.

3. Spreading of fluorosurfactant solutions on hydrocarbon substrates

As it was already mentioned the wetting properties of fluorosurfactants on hydrocarbon substrates are poorer than those of hydrocarbon surfactants with similar surface tension. According to [17] the spreading factor (the ratio of area wetted by the surfactant solution to that of water) on the parafilm for trisiloxane surfactant having the surface tension of 20.5 mN/m is about 8.6, whereas for fluorosurfactant FSB having lower surface tension of 18.8 mN/m the spreading factor is only 1.8.

We performed a study of wetting properties on the polypropylene film (PP) of two commercially available fluorosurfactants Novec FC-4430 (3M™) and Zonyl FSN-100 (DuPont™) having surface tension of 20 mN/m and 23 mN/m, respectively (see Table 2), close to that of commercial trisiloxane surfactant Silvet (~20 mN/m). Silvet wets completely the polypropylene film during around 1 min, with a spreading factor around 70 at a concentration of 0.5 g/l. Novec FC-4430 according to DuPont material safety data sheet is a blend containing 5–10% of polymers and 5% of organic solvents. It adsorbs rather slowly on the water/air interface according to the measurements of dynamic surface tension: equilibrium is attained only after 30 min at a concentration of 2 g/l being 10 times of the critical aggregation concentration (CAC) value. The spreading proceeds also much slower as compared with Silvet solutions, so that it is not completed even after 30 min (Fig. 2). After 30 min time the droplet retains its spherical shape with a contact angle of ~6 ° for a concentration of 5 g/l and ~16.5 ° for a concentration of 0.5 g/l. The spreading factor after 30 min is ~8.5 for a concentration of 5 g/l and ~4.5 for a concentration of 0.5 g/l, what is lower than the
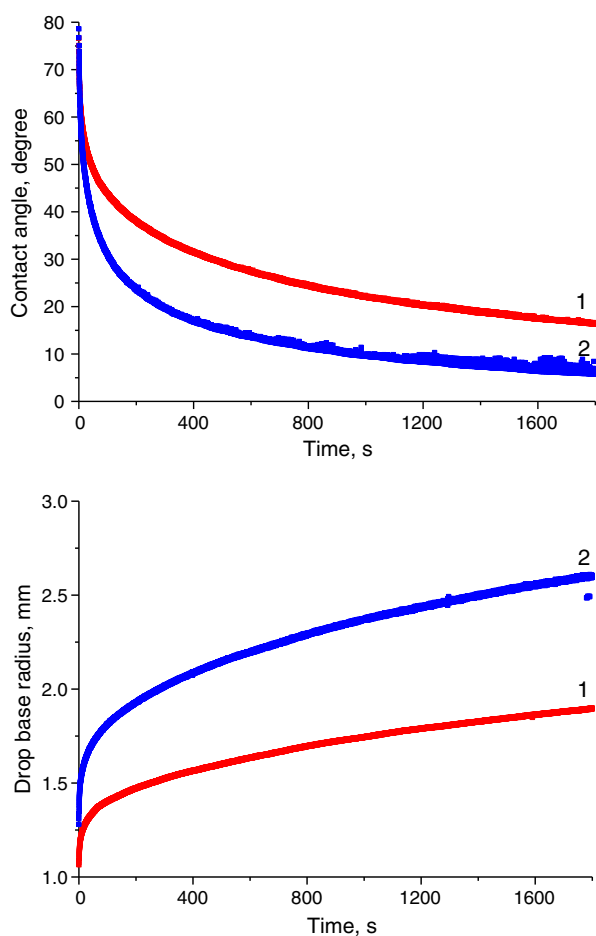
spreading factor of Silvet. The results presented in Fig. 2 were obtained at 100% humidity to prevent water evaporation; however, it was impossible to prevent the evaporation of organic solvents.

Fig. 2 shows that the time scale of spreading of Novec FC-4430 over hydrophobic substrate is roughly 30 times bigger as compared with the corresponding time scale of spreading of trisiloxane solutions. The latter substantial differences in time scales of spreading cannot be explained by difference in viscosities, which are almost identical for both solutions. As it was mentioned above Novec FC-4430 has a very slow adsorption kinetics at the liquid/air interface with a characteristic time of around 30 min. The latter is comparable with the rate of spreading in Fig. 2. Hence, it can be assumed that the rate of spreading is determined by a slow equilibration of surface tension at the three-phase contact line. Another possible mechanism has been proposed earlier [27]: spreading in this case is determined by a transfer of surfactant molecules on a bare hydrophobic substrate in front of the moving three-phase contact line (autophilic phenomenon). The latter process results in an increase of the solid–vapour interfacial tension of the hydrophobic solid surface in front of the moving three-phase contact line and spreading as a result. Transfer of surfactant molecules goes via high potential barrier and, as a result, the spreading is much slower than a 'hydrodynamic spreading'. The thorough theoretical analysis of spreading kinetics for this surfactant will allow allocating the proper spreading mechanism.

For solutions of Zonyl FSN-100 spreading completes during 2 min, but contact angles are higher than those of Novec FC-4430. The advancing contact angle value decreases with the increase of concentration and then levels off at critical wetting concentration (CWC). This minimum contact angle value for Zonyl FSN-100 on PP is ~35 ° which is higher than, for example, the minimum contact angle of the aqueous solution of tetraethylene glycol monodecyl ether, $C_{10}EO_4$, being ~20 ° [28], at higher surface tension of ~29 mN/m.

These examples demonstrate the better spreading properties of hydrocarbon surfactants vs fluorocarbon surfactants on hydrocarbon substrates. In what follows we discuss the possible causes of that phenomenon.

However, if the coverage of a hydrophobic surface should be made over much prolong period of time as compared with hydrocarbon surfactants, then fluorocarbon surfactant Novec FC-4430 is preferable as compared with trisiloxane solutions.

4. Adsorption of fluorosurfactants on the water/air interface

It was already mentioned earlier that fluorocarbons are much more hydrophobic than hydrocarbons and, therefore, fluorosurfactants are extremely surface active in aqueous solutions. According to [29] the incremental change in free energy of adsorption at the water/air interface per one CF_2 group is about −5.1 kJ/mol as compared to −2.6 kJ/mol for one CH_2 group. The bulk aggregation properties of fluorosurfactants are considered to be approximately equal to that of hydrocarbon surfactants of a similar structure and with similar hydrophilic part but with about 1.5 longer chains [2,30,31]. The fluorosurfactant has considerably higher surface activity than the hydrocarbon surfactant if we compare a pair having similar CMC and the free energy of micelle formation [29]. The Krafft temperature for ionic surfactants increases with the increase of the chain length and for perfluorinated (those containing only fluorocarbon groups) carboxylic acids and carboxylates with 12 and more CF_2 groups is higher than the room temperature [32]. As a consequence due to solubility limitations the chain length of perfluorosurfactants used in various applications usually does not exceed 10 CF_2 groups [33].

The Krafft point and the effectiveness (the maximum possible surface tension reduction [1]) of ionic perfluorinated surfactants depend essentially on the counterion used. Some results presented in [32] for perfluorocarboxylates and in [34] for salts of perfluoroalcanesulfonic acid are gathered in Table 1, which shows that the Krafft point for perfluorooctanoic acid (PFOA), $C_7F_{15}COOH$, is around 20 °C, that is all acids with longer chain precipitate at room temperature, whereas for

Fig. 2. Spreading kinetics of the aqueous solutions of Novec FC-4430 with concentrations of 1–0.5 g/l and 2–5 g/l on the polypropylene film.

Table 1
The Kraft point and effectiveness of perfluorocarboxylates [32] and salts of perfluoroalcanesulfonic acid [34].

Compound	Krafft point, °C	Minimum surface tension at 25 °C, mN/m
$C_6F_{13}COOLi$	Below 0	27.8
$C_7F_{15}COOH$	20	15.2
$C_7F_{15}COONa$	8.6	24.6
$C_8F_{17}COOH$	48.3	
$C_8F_{17}COOLi$	Below 0	24.6
$C_8F_{17}COONa$	24.6	21.5
$C_8F_{17}COONH_4$	10.6	14.8
$C_8F_{17}COONH_3C_2H_4OH$	Below 0	15.9
$C_{10}F_{21}COOLi$	Below 0	20.5
$C_{10}F_{21}COONH_4$	33	
$C_{10}F_{21}COONH_3C_2H_4OH$	18	13.8
$C_{12}F_{25}COOLi$	42	
$C_8F_{17}SO_3Li$	Below 0	29.8
$C_8F_{17}SO_3Na$	56.5	40.5[a]
$C_8F_{17}SO_3NH_4$	41	27.8[a]
$C_8F_{17}SO_3NH_3C_2H_4OH$	Below 0	21.5

[a]The measurement was performed at temperature below Krafft point; therefore the minimum surface tension corresponds to the solubility limit.

sodium perfluorooctanoate (SPFO), $C_7F_{15}COONa$, it is only 8.6 °C and it still remains below zero for the lithium salt $C_{10}F_{21}COOLi$. At the same time the minimum surface tension for PFOA is as low as 15.2 mN/m, whereas for SPFO it is already 24.6 mN/m.

The water/air surface tensions of commercially available fluorosurfactants are presented in Table 2. The data are taken from the manufacturer product information sheets. Unfortunately, the precise data on composition are usually not disclosed by the manufacturer; therefore only the type of the surfactant is presented. It should be noted that Capstone™ fluorosurfactants are proposed by DuPont™ as a replacement for Zonyl™ surfactants.

For comparison, the minimum surface tensions attained in the aqueous solutions of hydrocarbon surfactants are shown in Table 3.

The surface tension of fluorocarbons and therefore the surface activity of fluorosurfactants depend on the structure of surfactant molecules. According to [43] linear fluoroalkanes show the lowest surface tension, followed by the substituted and cyclic and aromatic fluorocompounds.

For partially fluorinated surfactants with terminal fluorocarbon segment adsorption is controlled mainly by the fluorinated part, whereas hydrocarbon groups demonstrate smaller surface activity as compared to that in purely hydrocarbon surfactants [43]. Study performed on a series of partially fluorinated surfactants with a dimorpholinophosphate polar head, a perfluoroalkyl terminal part and a hydrocarbon spacer has shown [44] that the free energy of adsorption at the water/air interface per one CH_2 group of these surfactants was about 2.5 times smaller than in hydrocarbon analogues. According to [44] such change in energy can be the result of folded conformation of hydrocarbon spacer, trying to conform to larger cross-sectional area of the fluorocarbon

part. Terminal hydrocarbon segments decrease the surface activity of the fluorosurfactant in aqueous solutions more than the internal hydrocarbon segment [1]. Replacement of only one fluorine with hydrogen in the terminal CF_3 group results in a substantial decrease of surfactant effectiveness. For example, the surface tension of sodium perfluorononanoate at CMC increased from 25.6 mN/m to 31.3 mN/m and that of sodium bis(1H,1H perfluoropentyl)-2-sulfosuccinate (double-tailed) from 17.7 mN/m to 26.8 mN/m by such replacement [45].

Most of commercial non-ionic fluorosurfactants are ethoxylates, but this is not the only option. Recently, for example, another series, perfluorinated sulfamates, was proposed [46] with minimum surface tension reached in aqueous solutions 15.7 mN/m.

The results presented above show clearly that fluorosurfactants are the most surface active water soluble substances considering the water/air interface and can lower the surface tension of aqueous solutions to 15–20 mN/m, whereas commonly used hydrocarbon surfactants lower it only to about 30–38 mN/m; their mixtures can lower the water/air interfacial tension to around 25 mN/m and double-tailed and trisiloxane surfactants are capable to lower the surface tension of aqueous solutions to 18–25 mN/m.

5. Adsorption of fluorosurfactants on water/oil and water/hydrophobic solid interfaces

It is much easier to study the effect of surfactant on the interfacial tension of the water/oil than that of the water/solid interface because the former can be measured directly whereas the latter can be only found by indirect methods, for example using the data on the amount of the adsorbed surfactant. On the other hand there is also a complication related to the water/oil interface for the case of non-ionic surfactants, because they are usually soluble in the oil phase; therefore the precautions have to be made to be sure that the equilibrium interfacial tension is measured and also the equilibrium bulk concentration in water has to be determined after the partition equilibrium is established. Measurement of interfacial tension with ionic surfactants is easier because they are almost non-soluble in the non-polar oil phase and their initial concentration in water can be considered as an equilibrium one.

The comparative study of the interfacial tension of the diluted solutions of sodium alkylsulfates and sodium perfluoroalcanoates against air, hexane and perfluorohexane was performed in [29]. Below we mostly consider the results concerning sodium perfluorooctanoate (SPFO) and sodium decylsulphate (SDeS) having similar CMC and close free energy of micelle formation [29]. At relatively low concentrations the interfacial tensions decrease linearly with concentration [29]. The slope of this dependency is the measure of affinity of a surfactant to the interface. According to [29] the fluorosurfactant, SPFO, causes much larger lowering of surface tension at the water/air and water/perfluorohexane interface, but much smaller at the water/hexane interface in comparison to the hydrocarbon surfactant SDeS (Table 4).

The free energy of adsorption differs very much for fluoro- and hydrocarbon surfactants on various interfaces according to [29] (see also

Table 2
Surface tension of the aqueous solutions of commercially available fluorosurfactants.

Surfactant	Type	Minimum surface tension at 25 °C, mN/m	Manufacturer
Novec FC-4430, FC-4432, FC -4434	Non-ionic, polymeric	20	3 M™
FC-5120	Anionic, ammonium fluoroalkylsulfonate	19	3 M™
Zonyl FSN-100	Non-ionic, ethoxylate	23	DuPont™
Zonyl FS-300	Non-ionic, ethoxylate	23	DuPont™
Zonyl FS-500	Amfoteric, betaine	15.5	DuPont™
Capstone FS-10	Perfluoroalkylsulfonic acid	20	DuPont™
Capstone FS-30	Non-ionic, ethoxylate	21	DuPont™
Capstone FS-60	Anionic, blend	19	DuPont™
Capstone FS-61	Anionic, phosphate	20	DuPont™
Capstone FS-63	Anionic, phosphate	19	DuPont™
Capstone FS-64	Anionic, phosphate	17	DuPont™
Capstone FS-65	Non-ionic	18	DuPont™

Table 3
Surface tension of the aqueous solutions of hydrocarbon surfactants.

Surfactant	Type	The surface tension at CMC at room temperature, mN/m	Reference
Sodium dodecyl sulphate (SDS)	Anionic	38	[35]
Dodecyltrimethyl-ammonium bromide (DTAB)	Cationic	38	[35]
Hexadecyltrimethyl-ammonium bromide (CTAB)	Cationic	37	[36]
Oxyethylated alcohols	Non-ionic, ethoxylated		[37]
$C_{14}EO_8$		33	
$C_{12}EO_5$		30	
$C_{10}EO_4^a$		29	
SDS + DTAB	Mixture, anionic + cationic	25	[35]
Dimethyldidodecyl-ammonium bromide (DDAB)	Cationic, double Tailed	18	[38]
		22.6	[39]
		24.5^a	[40]
Trisiloxanes $((CH_3)_3SiO_2)_2Si-(CH_3)(CH_2)_3(OCH_2CH_2)_nOH$ $n = 4–12$	Non-ionic, ethoxylated	20–21	[41,42]

^{a} According to our measurements.

two last columns in Table 4). However, the values of limiting adsorption are very close for both surfactants at water/air, water/perfluorohexane, and water/hexane interfaces. Therefore, it can be concluded that the difference in the maximum changes of the interfacial tension is mostly due to differences in the adsorption energy rather than in the adsorbed amount of surfactant. The incremental change in the free energy of adsorption per one CF_2 group is larger than that per one CH_2 group even for the water/hexane interface, although this increment is lower than for two other interfaces, whereas for the CH_2 group the increment at the water/hexane interface is the highest according to [29] (Table 5).

The results obtained in [29] are in good agreement with the other data published. So, according to the Table 1 the minimum surface tension attained by the SPFO ($C_7F_{15}COONa$) aqueous solution (24.6 mN/m) is much lower than that of the SDeS solution (38 mN/m), whereas the minimum interfacial tension against hexane is much lower for the SDeS solution (5 mN/m) than for the SPFO solution (14 mN/m) (see Table 6). Note, in Tables 3 and 6 the data for SDS instead of SDeS are given, but usually the minimum surface tension is rather similar inside the series of surfactants, see for example the data for alkyltrimethylammonium bromides in [36].

The comparison of the results presented in Tables 1, 3 and 6 demonstrate, that although fluorosurfactants are more effective in comparison to the hydrocarbon ones at the water/air interface they are often less effective at the interface between aqueous solution and hydrocarbon liquid interface. As the spreading coefficient depends on the sum of liquid/vapour and substrate/liquid interfacial tension this sum can be smaller for trisiloxane or double-tailed hydrocarbon surfactants in comparison to fluorosurfactants despite the higher surface tension of their aqueous solutions.

It was already mentioned above that the mixtures of anionic and cationic hydrocarbon surfactants demonstrate synergetic effect, lowering surface tension to smaller values than the individual components (see the data on SDS, DTAB and their mixture presented in Table 3). The pronounced synergetic effect for the mixtures of hydrocarbon and fluorocarbon ionic surfactants has been proven in [48]. Some data from this work are presented in Table 7. It was shown in [48] that the lowering of values of interfacial tension using the mixtures resulted in transition from partial to complete wetting. Note, the concentrations

studied in [48] are below CMC, that is why the values of surface/interfacial tension differ from those given in Tables 1 and 6. The minimum surface and interfacial tension for octyltrimethylammonium bromide (OTAB) are similar to those for CTAB.

In the case of the water/oil interface the hydrophobic part of the surfactant molecule is submerged into the oil phase and, therefore, its interactions with the molecules of the oil phase are of importance. This is confirmed by the differences in the free energy of adsorption presented in Table 4. Obviously, interaction with solid substrate will be different from that with liquid substrate even with similar composition. Still one can expect some similarity, especially in affinity between hydrocarbon and fluorocarbon compounds.

Unfortunately, there are no direct methods to measure the interfacial tension at the interface between the solid and aqueous solutions. The only data on adsorption are available as to our knowledge. The indirect method based on the Young Eq. (1) is often used to estimate σ_{sl} and σ_{sv} interfacial tensions. In this method the liquid/vapour surface tension and contact angle are measured directly. To find two unknown values σ_{sl} and σ_{sv} one more equation is needed. This second equation can be chosen in various ways (see discussion in [22] and references herein) and this choice influences the result obtained. We will not discuss here the results obtained by this method, because the aim of this paper is to consider the reverse problem—how to estimate the wetting properties of solutions.

The similar indirect approach based on the work of Lucassen-Reinders [51] is also used to find the adsorbed amount of surfactant. Combination of the Young Eq. (1) and the Gibbs adsorption isotherm results in

$$\frac{d\sigma_i}{dln(a)} = -RT\Gamma_i, \qquad (3)$$

where a is the activity (can be replaced by concentration at small concentrations), R is the gas constant, T is the temperature, and Γ is the adsorption. It is possible to get using Eq. (3) that

$$\frac{d(\sigma_{lv}cos(\theta))}{d\sigma_{lv}} = \frac{\Gamma_{sv}-\Gamma_{sl}}{\Gamma_{lv}}. \qquad (4)$$

Table 4
The slope $d\sigma/dC$ (σ is the interfacial tension, C is the concentration) and free energy of adsorption, ΔG, for SPFO and SDeS at various interfaces [29].

Interface	$-d\sigma/dC$, mN/m/mol		$-\Delta G$, kJ/mol	
	SPFO	SDeS	SPFO	SDeS
Water/air	$8.86 \cdot 10^3$	$1.36 \cdot 10^3$	47.5	38.4
Water/hexane	$9.8 \cdot 10^3$	$1.97 \cdot 10^4$	48.6	51.9
Water/perfluorohexane	$2.7 \cdot 10^4$	$4.32 \cdot 10^3$	53.5	44.5

Table 5
Incremental changes of the free energy of adsorption CF_2 and CH_2 groups on various interfaces [29].

Interface	$-\Delta\Delta G$, kJ/mol	
	CF_2	CH_2
Water/air	5.10	2.59
Water/hexane	5.06	3.43
Water/perfluorohexane	5.36	2.89

Table 6
Interfacial tension of various surfactants at water/hydrocarbon interfaces.

Surfactant	Interface	The interfacial tension at CMC, mN/m	Reference
Fluorosurfactants			
SPFO	Hexane	14	[47]
PFOA	Heptane	7.6	[48]
T-1	Octane	4.5	[49]
T-1	Decane	6.8	[49]
T-1	m-Xylene	6.2	[49]
Hydrocarbon surfactants			
SDS	Hexane	5	[50]
CTAB	Hexane	5	[36]
DDAB	Octane	0.1	[38,39]
Trisiloxanes	Tetradecane	<1	[41]

As a rule Γ_{lv} can be found from the isotherm of surface tension. In [51] Γ_{sl} has been found from the mass balance of surfactant and Γ_{sv} was found from Eq. (4).

Below we consider the only data obtained from the direct measurements. Adsorption of SPFO and SDeS on Graphon was studied in [52] for concentrations below CMC. It was shown that at concentrations close to CMC the adsorbed amount of SPFO is slightly higher than that of SDeS, adsorbed amounts are equal at 0.5 CMC and adsorption of SDeS is much higher at small concentrations. If one accepts that the free energy of adsorption follows the same trend as for liquid interfaces, it could be expected that the solid/liquid interfacial tension is lower for the interface with the SDeS solution. It is noteworthy that adsorption of SPFO on Graphon at CMC was very close to that at the water/air interface, whereas adsorption of SDeS was slightly lower.

Adsorption of partially fluorinated cationic Gemini surfactants with dimethylammonium bromide hydrophilic head and hydrocarbon spacer (either C_6 or C_{12}) as well as the corresponding single chains on water/air, water/hydrophilic silica and water/octadecyltrichlorosilane (OTS) interfaces was studied in [53] by neutron reflectometry. The surface tension at the water–air interface was in the range of 27–33 mN/m, whereas the surface tension of single chain varied between 20 and 25 mN/m. The value of area per molecule found in this study for surfactant concentrations close to CMC is presented in Table 8. According to these data the area per molecule remains practically constant at the water–air interface, whereas it increases with the increase of the fluorinated part at the water/OTS interface and for the longest fluorinated part, FC_8 it becomes larger (i.e. adsorbed amount decreases) than at the water/air interface.

Examples discussed above allow assuming that fluorosurfactants adsorb at the interface between their aqueous solution and hydrocarbon solid in amounts comparable to their adsorption liquid/air interface, as the hydrocarbon surfactant does. Nevertheless, adsorption of fluorocarbon surfactants results in smaller changes of water/hydrocarbon interfacial tension in comparison to adsorption of hydrocarbon surfactants, because of smaller free energy of adsorption.

6. Adsorption on the substrate/air interface

If an oil soluble surfactant is used to facilitate the spreading on a water/oil interface, not only oil/water, but also the oil/air interfacial

Table 7
Surface, ST, and interfacial (water/heptane), IT, tensions of mixtures of SPFO and OTAB [48].

Concentration of SPFO, mM	Concentration of OTAB, mM	ST, mN/m	IT, mN/m
4.18	0	47.0	31.3[a]
2.09	2.09	14.7	0.4
1.05	1.05	15.0	0.4
0.643	0.643	18.4	1.0
1.39	2.78	14.9	0.4
0.836	3.34	14.9	0.4

[a] Water/kerosene interface.

Table 8
Area per molecule for partially fluorinated Gemini surfactants adsorbed at water/air and water/OTS interfaces [53].

Surfactant	Area pro molecule, A^2	
	Water/air	Water/OTS
$(fC_4C_{11})_2$-C_6	106	89
$(fC_5C_{10})_2$-C_6	106	89
$(fC_6C_8)_2$-C_6	105	90
$(fC_8C_6)_2$-C_6	108	120

tension can change and this change should be taken into account, especially in the case of fluorosurfactants which can considerably decrease the surface tension of many organic liquids [1]. In this case the substrate/air surface becomes even more hydrophobic and therefore larger decrease in the water/air and oil/water tension is needed to facilitate spreading.

The question remains open whether there is adsorption of surfactant on solid/vapour interface or on oil/vapour interface in the case of the surfactant insoluble in the oil phase. It is generally accepted that there is adsorbed films of molecules of pure liquid [54] or a surfactant [55] on a hydrophilic interface ahead of three phase contact line hindering the spreading of low energy liquids over high energy solids, the phenomenon called autophobic effect. Note, those films should not be confused with the precursor films on the leading edge of spreading droplet [56]. To distinguish between them in experimental studies is also a challenge. The adsorbed films of volatile liquids are formed mostly by adsorption from the vapour [54], whereas for surfactant solutions the surface diffusion should be important. An autophobic effect was not observed when the ionic surfactant used had the same charge as a surface [55]. It should be stressed that autophobic effect is linked to the decrease of the energy of the solid/vapour interface due to adsorption.

Possible adsorption of the surfactant ahead of three phase contact line on hydrophobic interfaces (making them hydrophilic) is considered as an autophilic effect facilitating the spreading of the surfactant solution on the low energy solid [27,57–59]. The idea appeared first to explain the kinetics of spontaneous imbibition of the surfactant solution in hydrophobic capillaries [57] and then the kinetics of spreading of droplets of surfactant solutions over hydrophobic substrates [58]. The region of higher wettability ahead of the three phase contact line was observed in [59] by condensation figure imaging. The decisive direct experimental evidence of the presence of surfactant molecules in front of the moving three-phase contact line on a hydrophobic surface has been provided in [59].

Considering the solutions of fluorosurfactants on hydrocarbon substrates it could be expected that autophilic effect should be less pronounced for them, because of smaller energy of interaction between hydrocarbon and fluorocarbon groups and therefore larger energy barrier for adsorption. On the other hand, to explain the worse wettability of hydrocarbon surfaces by fluorosurfactant solutions it was assumed that autophobic effect can take place in this case, i.e. surfactant molecules adsorb ahead of a three phase contact line with fluorocarbon tails exposed to the air, lowering the energy of solid/vapour interface and hindering spreading in this way [21]. Therefore, it is a question to be answered, whether the fluorosurfactants adsorb ahead of the three phase contact line by deposition of their solution on the hydrocarbon substrate and if so, do they make the surface more hydrophilic or more hydrophobic.

7. Conclusions

Fluorosurfactants are the most effective compounds to lower the surface tension of aqueous solutions, but their wetting properties as related to low energy hydrocarbon solids are inferior to hydrocarbon surfactants, although the latter demonstrate higher surface tension in aqueous solutions. One of the reasons is most probably the lower free

energy of adsorption of fluorosurfactants on the hydrocarbon solid/ water interface, but more thorough systematic study on this subject is required. Another question to be answered is whether fluorosurfactants adsorb on the solid/vapour interface ahead of three phase contact line and if they do, whether this facilitates or hinders the spreading.

Mixtures of ionic fluoro- and carbohydrate surfactants demonstrate outstanding synergetic effect and facilitate spreading over hydrocarbon oil surfaces. Therefore another problem to be addressed is to expand those studies to other types of surfactants, including commercial ones and to solid/liquid interfaces.

Acknowledgments

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