Wetting dynamics of polyoxyethylene alkyl ethers and trisiloxanes in respect of polyoxyethylene chains and properties of substrates

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Metadata Record: https://dspace.lboro.ac.uk/2134/25802

Version: Published

Publisher: © Elsevier

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Wetting dynamics of polyoxyethylene alkyl ethers and trisiloxanes in respect of polyoxyethylene chains and properties of substrates

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**Abstract**

Wetting performance of aqueous solutions of trisiloxane surfactants (TEOₙ) and polyoxyethylene alkyl ethers (CₙEOₙ) on polypropylene, Parafilm and Teflon AF surfaces in a wide range of concentrations has been investigated. Surfactants CₙEOₙ only facilitate partial wetting of water on all surfaces, but TEOₙ surfactants induce superspreading on polypropylene and Parafilm at room temperature (22 °C) at critical wetting concentration (CWC). Influence of the length of EO chains on wetting ability has a completely different character for CₙEOₙ and TEOₙ surfactants. In the case of CₙEOₙ, the final contact angle increases on all substrates used with increasing number of EO units. However, the final contact angles for droplets of TEOₙ solutions decrease with increasing of n(EO) reaching a minimum values at n(EO) = 6 at the critical aggregation concentration (CAC), or show complete spreading (the final contact angle is nearly zero) for n(EO) = 5–8 at 1 CWC on moderately hydrophobic substrates. Temperature-dependent spreading behaviour of both TEOₙ and CₙEOₙ surfactant solutions has also been studied. It has been shown for the first time, that tuning of spreading performance with temperature for polyoxyethylene alkyl ether surfactants is possible. The increase of spreading capability for both trisiloxane surfactant solutions and polyoxyethylene alkyl ethers solutions is observed at temperature close to the cloud point for a given surfactant.

**Keywords:** Surfactant, Spreading, Hydrophobic surfaces, Trisiloxanes, Polyoxyethylene alkyl ethers

**Graphical Abstract**

**Highlights**

- Spreading of aqueous solutions of trisiloxanes and polyoxyethylene alkyl ethers.
- Wetting of Parafilm and Teflon AF surfaces in a wide range of concentrations.
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**Article Info**

Article history:
Received 10 February 2012
Received in revised form 18 April 2012
Accepted 24 April 2012
Available online 11 May 2012

**Keywords:** Surfactant, Spreading, Hydrophobic surfaces, Trisiloxanes, Polyoxyethylene alkyl ethers

**1. Introduction**

The improvement of spreading ability of water-based solutions over hydrophobic surfaces is of great importance in such industrial processes as herbicide spreading [1–3], paper and plastic recycling processes [4,5], and other applications [6]. To enable water to spread over low-energy substrates surfactants are used as additives decreasing the interfacial tension of air–water and solid–water interfaces through energetically favourable adsorption of surfactant molecules at these interfaces.

Nonionic ethoxylated alcohols (polyoxyethylene alkyl ethers, CₙEOₙ) can lower the surface tension of aqueous solutions down to 30 mN/m [1,7] at the CMC and facilitate wetting of hydrophobic surfaces. Spreading behaviour of aqueous solutions of the homologues C₄EOₙ over hydrophobic surfaces have appeared to be the
most studied in the literature [8–12] compared to, for instance, the homologues C_{10}EO_{n}. It was found that the droplets of C_{12}EO_{n} surfactant solutions facilitate spreading of aqueous solutions on moderately hydrophobic surfaces, while on highly hydrophobic surfaces spreading is not observed [12]. Increasing the length of the EO chain decreases spreading capability of those surfactant solutions on more hydrophobic surfaces; the latter is caused by a loose packaging of molecules on interfaces caused by repulsion between EO chains. Droplets of surfactant solutions reach constant quasi-equilibrium final contact angles with increasing concentration above the CMC [9,10].

Another class of widely used nonionic surfactants are trisiloxane surfactants (TEOₙ) consisting of silicone-based hydrophobic moiety with methyl groups [1,2]. Both trisiloxanes and polyoxyethylene alkyl ether surfactants have identical ethylene oxide (EO) hydrophilic groups. However, despite of that similarity trisiloxanes are capable of promoting a rapid spreading of aqueous droplets over moderately hydrophobic surfaces and wet them completely at high concentrations [2,3,13–15]. This phenomenon is frequently referred to as “superspreading” [2,3,13–15]. In aqueous phase trisiloxane monomers spontaneously form bilayer and vesicle as the concentration of monomers exceeds the critical aggregate concentration (CAC) and decrease the water–air interfacial tension down to 20 mN/m [1,2]. It was found [16,17] that trisiloxanes possess an extra critical concentration known as the wetting concentration (CWC) above which superspreading phenomenon takes place [16,17]. The CWC is several times higher than the CAC; however, no change in the water–air interfacial tension at concentrations above CWC was detected. It was shown in [17,18] that the droplets of surfactant solutions reach a constant final contact angles at concentrations above CWC (C ≥ CWC). Using atomic force microscopy Svitova et al. [16] showed that at C ≥ CWC multilayer aggregates appeared on hydrophobic solids several hours after the deposition of solutions. These aggregates were suggested by authors to be responsible for superspreading behaviour of trisiloxanes. No multilayered aggregation occurs for ethoxylated alcohol at the solid–solution interface. FTIR-ATR spectroscopy study [19] showed that absorbance of trisiloxanes at the solid–solution interface in a trough continuously increases with concentrations, whereas for ethoxylated alcohol the absorbance reaches a constant value at C ≥ CMC. A number of authors [20–23] speculated that superspreading behaviour of trisiloxanes could be determined by the phase-state of their aqueous solutions, when vesicles, lamella and/or sponge phase form at specified temperature conditions. However they studied the phase behaviour of trisiloxanes at very high concentrations [20–23] while the superspreading was observed at concentrations just around 0.1 wt.% [13]. Wagner et al. [23] investigated temperature-dependent spreading of trisiloxanes and their phase behaviour at concentrations from 0.1 to 5 wt.%. According to their results the initial spreading rate of trisiloxanes is strongly influenced by temperature. If the temperature of the solution is slightly above a cloud point (CP) at which surfactant solutions separate into the two coexisting liquid phases: one phase is water containing monomers, and the other phase contains mostly structured aggregates), then increasing the spreading rate as compared with the initial spreading rate is detected.

The temperature-dependent phase behaviour of polyoxyethylene alkyl ethers has drawn attention of many authors [7,24,25] for many years. Surprisingly no results have been reported on temperature-dependent spreading of these surfactants on hydrophobic solids.

There are a few papers available where comparison of spreading characteristics of a limited number of polyoxyethylene alkyl ethers and trisiloxanes surfactants in respect of concentration and energy of surfaces reported [18,26,27].

Below we presented results of systematic comparison of spreading behaviour of alcohol ethoxylated C_{10}EO_{n} where n(EO) = 3–8 and trisiloxanes TEOₙ where n(EO) = 4–9 depending on concentration of surfactants, the length of the oxyethylene (EO) chains, properties of polymer substrates and temperature. Some data on behaviour of aqueous trisiloxane solutions have been taken from our previous works [17,18].

2. Experimental

Nonionic ethylene glycol monodecyl ether surfactants, chemical formula CH_{3}(CH_{2})_{9}(OCH_{2}CH_{2})_{n}OH, further referred to as C_{10}EO_{n}, where n = 3–6, 8 ethylene oxide (EO) groups and poly(4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene) also known as Teflon AF were purchased from Sigma–Aldrich, UK. Monodisperse trisiloxane surfactants were kindly provided by Dr R M Hill, DowCorning, USA. Polypropylene film was kindly supplied by Dr. J. Venzmer, Evonik Industry, Germany. Parafilm® M sealing film was purchased from Fisher Scientific, UK. Solvent Fluorinert FC-75 was purchased from 3 M, UK.

Polypropylene (PP), Parafilm (PF) films and silicon wafer hydrophobized with Teflon AF (TF) polymer were used in our experiments as substrates showing different solid–air interfacial energies in terms of contact angles of pure water [17]: (97 ± 1)° on PP, (106 ± 2)° on PF, and (117 ± 1)° on TF. Silicon wafers were hydrophobized using Teflon AF in the following way. Teflon AF polymer 0.5 g was dissolved in 200 mL of Fluorinert F75 solvent. The silicon wafer plates (1 cm⁻²) were carefully cleaned according to the following protocol: 30 min ultrasonication in isopropyl alcohol then rinsed in distilled water and soaked in chronic acid for 1 h, intensive rinsed in distilled and DI water, and then dried in a strong jet of compressed air. Cleaned and dried silicon wafers were stored in a Petri dish. Solution of Teflon AF was carefully deposited on each plate. Petri dish was covered to avoid settling dust particles on Teflon AF covered wafers surface. Plates were left overnight to evaporate the solvent. PP and PF polymer films were washed with isopropyl alcohol, then rinsed in DI water and dried with jet of compressed air. Data on the critical micelle concentration (CMC) for C_{10}EO_{n} surfactants were collected from the literature and presented in Table 1. Aqueous solutions of C_{10}EO_{n} surfactants at concentrations varying from 0.1 CMC to 4 CMC were prepared using ultra pure water (Millipore filter 18.2 MΩ cm). Some data for trisiloxanes TEOₙ with n(EO) = 4, 6, 8, 9 and commercially available trisiloxane Silwet L-77 were taken from [17,18] and adapted to an

### Table 1

Critical concentrations of used surfactants. The uncertainty in the CAC is ±0.003 mmol/L.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>CMC mmol/L</th>
<th>C_{10}EO_{3}</th>
<th>C_{10}EO_{4}</th>
<th>C_{10}EO_{5}</th>
<th>C_{10}EO_{6}</th>
<th>C_{10}EO_{7}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silwet L-77</td>
<td>0.094</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEOₙ</td>
<td>TEO₆</td>
<td>TEO₅</td>
<td>TEO₄</td>
<td>TEO₃</td>
<td>TEO₂</td>
<td>TEO₁</td>
</tr>
<tr>
<td>CAC mmol/L [17,28]</td>
<td>0.22</td>
<td>0.028</td>
<td>0.061</td>
<td>0.11–0.17 [3,32]</td>
<td>0.094</td>
<td>0.15</td>
</tr>
<tr>
<td>CWC mmol/L [17]</td>
<td>0.312 ± 0.05</td>
<td>0.05±</td>
<td>0.527 ± 0.03</td>
<td>0.4 ± 0.01</td>
<td>0.698 ± 0.08</td>
<td>0.613 ± 0.12</td>
</tr>
</tbody>
</table>

* CWC for TEOₙ were estimated from dependencies of CWC vs. number of EO units plotted for known values for TEOₙ.
approach used below. All experimental procedures are the similar to those described above. The data on the critical aggregation concentration (CAC) and the critical wetting concentration (CWC) for trisiloxanes are presented in Table 1.

Dropets of surfactant solutions were deposited on polymer plates with a precision syringe inside of a closed chamber. The chamber was used to create and strictly control the required experimental conditions. The chamber with water jackets was used to fix temperature inside the cell. Prior to each experiment the cell with solutions were kept at the fixed temperature until equilibration. The experiments were conducted at the following conditions: at room temperature ($T = 22 \pm 1 ^\circ C\), RH = 75 $\pm$ 5% for both ethylene glycol monododecyl ether surfactants and trisiloxanes; at low temperature ($T = 5 \pm 2^\circ C\), RH = 50 $\pm$ 5% for trisiloxanes with n(EO) equals to 4, 8, 9, and tetraethylene glycol monododecyl ether (C10EO4); at high temperature ($T = 75 \pm 5^\circ C$) for hexaethylene glycol monododecyl ether (C10EO6). The temperature conditions different from a room temperature were selected corresponding to the cloud point temperature of the mentioned surfactants to test influence of the phase conditions on spreading ability of the surfactant solutions (see Section 3). Volumes of all droplets used were around 3 $\mu$L and 2 $\mu$L that allowed neglecting the gravity action. The side view of the spreading process was captured using a CCD camera at 30 fps. Captured images were analyzed using Drop tracking and analysis evaluation software (Micropore Technologies, UK) to monitor the time evolution of the spreading diameter, height, radius of curvature, and contact angle of spreading droplets. At room and low temperatures the change of droplet volume caused by evaporation during the whole spreading process was less 5%. At high temperature ($T = 75 \pm 5^\circ C$) droplets loose ~10% of their initial volume in 15–20 s after a deposition on substrate. The experiments were repeated 5–8 times to control the reproducibility. Contact angles were measured with the error 1–3°.

3. Results and discussion

3.1. Advancing contact angle evolution of ethoxylated alcohols, C10EO

An advancing contact angle of any droplet used gradually decreased due to spreading from an initial value of the contact angle ($\theta_0$) measured immediately after the droplet deposition on the substrate to a certain quasi-equilibrium or a final value ($\theta_{\infty}$) after which no further spreading occurred (Fig. 1). Three modes of spreading of homologous C10EO n over different polymeric substrates can be identified from the experiments (see Fig. 1): (i) non-wetting mode when both $\theta_0$ and $\theta_{\infty}$ were above 90°. The latter was found for ethoxylated alcohols with n(EO) = 3 and n(EO) = 8 at C = 0.1 CMC on Teflon AF; (ii) transition from nonwetting ($\theta_0 > 90^\circ$) to partial wetting ($\theta_{\infty} < 90^\circ$) observed for all C10EO n at concentration ranging in (0.1–0.3) CMC on Teflon AF; and finally (iii) partial wetting ($\theta_0 < 90^\circ$ and $\theta_{\infty} < 90^\circ$) was detected for all other cases. No transition from partial to complete wetting was found for surfactant homologous C10EO n at concentrations even much higher than CMC on all substrates (Teflon AF, Parafilm, polystyrene) studied.

Fig. 2(a–c) shows dependencies of the final contact angles $\theta_{\infty}$ on concentration of C10EO n surfactants on all substrates studied. This shows that $\theta_{\infty}$ decreases with increasing concentration until the CMC is reached. Above the CMC the final contact angles $\theta_{\infty}$ attain more or less constant values. This trend is consistent with the results obtained by other authors for nonionic and anionic surfactants on different hydrophobic surfaces [9–11,17,18]. These findings can be used as a simple method for estimation of CMC values for nonionic surfactants: just a searching for a cross-section point of the fitted straight lines on a log–log plot similar to that of CWC for trisiloxanes [17]. However, Drelich et al. [8] found that the transition point for C2EO n surfactants on PP and toner surfaces appeared at concentrations few times larger than the CMC. According to the authors the shift of transition point could be explained by the deplet of the surfactant in the bulk of the droplet and by the formation of different molecular configurations at the hydrophobic surface at different surfactant concentrations [8].

Fig. 2 shows that more hydrophilic surfactants with n(EO) = 6, 8 demonstrate lower wetting ability in comparison with surfactants having short EO chains, n(EO) = 3–4, regardless of the surface energy of substrates (PP, PF and TF) studied.

All polyoxymethylene alkyl ether surfactants studied demonstrate better spreading performance on polypropylene surface with mostly –CH$_3$ solid surfaces groups as compared to Teflon AF surface having –CF$_3$ solid surfaces groups that is a complete agreement with Zisman' sequence [33]: hydrophobicity of surface groups decreases as follows: CF$_2$ > CF$_2$ > CH$_3$ [33].

Fig. 3 shows dependency of the final contact angles ($\theta_{\infty}$) for droplets of aqueous solutions of C10EO n on the number of EO groups at the CMC. It is appeared that increasing of the EO length results in an increase of $\theta_{\infty}$, that is, the spreading capability of surfactants become lower. Decrease of a density of monomers adsorbed on the solid surface with an increase of the length of EO chains is one of possible explanations for this behaviour. The latter could be due to (i) increase of the area required for a molecule to be adsorbed. It was shown in [29] that the area per molecule for C10EO n at solid–liquid interface increases from 34 A$^2$ for C10EO4 to ~60 A$^2$ for C10EO6; (ii) repulsion between hydrophilic parts of neighbouring molecules results in a loosely packaging of monomers. However, we suggest that this tendency could also be due to temperature-dependent phase behaviour of solutions of ethoxylated alcohols with different length of EO chains (see Section 3.3 below).

3.2. Advancing contact angle evolution of ethoxylated trisiloxanes, TE0

It was shown above that ethoxylated alcohol surfactants show three modes of spreading. However, trisiloxane surfactant solutions show four modes of spreading depending on the surfactant concentration and the energy of substrates (Fig. 4): (i) completely non-wetting (at low concentrations on Teflon AF); (ii) transition from nonwetting ($\theta_0 > 90^\circ$) to partial wetting ($\theta_{\infty} < 90^\circ$); (iii) partial wetting only (both $\theta_0 < 90^\circ$ and $\theta_{\infty} < 90^\circ$); (iv) transition at intermediate concentrations on all three solid substrates investigated; and at last (iv) complete wetting or superspreading at C $\approx$ CMC on moderately hydrophobic surfaces (PF and PP) in the
case of relatively long \( n(EO) = 6–9 \) chains [17] (see Fig. 4). The spreading modes (i)–(iii) are similar to those of nonionic ethoxylated alcohol surfactants and anionic/ionic surfactants on slightly hydrophobic substrates [9–11], but the mode (iv) is attributed to trisiloxane surfactants only. It is well recognized now that the behaviour (iv) does not related to the capability of trisiloxanes to decrease the surface tension to a low value (20 mN/m), because fluorocarbon surfactants can decrease the surface tension of water down to 18 mN/m but do not show complete spreading on moderately hydrophobic surfaces [3,34].

Fig. 2. (a–c) Final contact angles for droplets of aqueous solutions of alkyl polyoxyethylene ethers vs. concentration on different polymeric substrates at room temperature. Vertical straight lines show points of inflection corresponding to 1 CMC.

Fig. 3. Final contact angles at 1 CMC vs. number of ethylene oxide unites (EO) for alkyl polyoxyethylene surfactants on substrates: Teflon AF (TF) –; Parafilm (PF) –; and polypropylene (PP) –.

Fig. 5a and b shows the dependency on concentration of the final contact angle of trisiloxanes studied on all substrates (some data adopted from our previous results [17,28,35]). It is seen the special feature of trisiloxanes compared to alkyl polyoxyethylene ethers: the transition point on the plots of \( \theta_\text{m} \) vs. concentration takes place at concentrations a few times higher than the CAC. The concentration corresponding to the transition point is referred to as a critical wetting concentration (CWC) [16,17,26].

There is a substantial difference between CAC and CWC concentrations: the CAC corresponds to the lowest surface tension at a liquid–vapour interface, while the CWC characterizes the limit of their spreading capability. Important to emphasises that CWC does not depend on the degree of hydrophobicity of substrates [16,17].

Fig. 6 shows the dependency of the final contact angle of TEO\(_n\) on the number of EO groups at CAC and CWC. Again, it is clearly seen the substantial different character of these dependencies as compared to those for C\(_{10}\)EO\(_n\) surfactants. The final contact angle decreases with the length of EO group and reaches zero or close to zero values for relatively long chains \( n(EO) = 6–9 \) at concentration \( > 1 \) CWC. The latter behaviour is in the contradiction with a concept of an increase of the area of packaging vs. the length of EO chains, which is seems to be valid for alkyl polyoxyethylene ethers surfactants. More than that, Gentle and Snow [36] showed that adsorption of trisiloxanes at liquid-vapor interface does not vary with the EO length within the range of \( n(EO) = 4–16 \).

Ruckenstein [37] concluded theoretically that trisiloxanes with intermediate length of EO chains, \( n(EO) = 7–8 \), able to stimulate high spreading capability of water on hydrophobic surfaces, whereas an
increasing the EO length leads to a lower adsorbability of surfactants at interfaces because of strong attraction interaction with water and reduces spreading efficiency. However, no attention has been paid to very efficient wetting behaviour of TEO₅, which is in some cases similar to that of TEO₆ and TEO₉.

3.3. Influence of temperature on spreading behaviour of ethoxylated alcohols and trisiloxane surfactant solutions

3.3.1. Trisiloxane surfactants

Wagner et al. [23] investigated temperature-dependent spreading rate of the homologous trisiloxanes and found that trisiloxanes with n(EO) = 4 drastically increases the initial spreading rate when temperature decreases down to 6 °C, which is close to its the CP temperature. The initial spreading rate of trisiloxanes with n(EO) = 6 and 9 do not changes remarkably with temperature varying from 6 °C to 26 °C [23], but TEO₆ shows a best spreading performance in compare to TEO₉ at both temperatures.

As we showed above that at temperature ~20 °C solutions of TEO₄ do not show considerable spreading on all surfaces, but TEO₆ does it (see Fig. 6). Below we compare experimental results on spreading kinetics of 1 CWC solutions of TEO₄, TEO₆ and TEO₉ at both low (Tᵢ = 5 ± 2 °C) and room (Tᵢ = 22 ± 1 °C) temperatures on all substrate used.

Fig. 7 shows an evolution of the advancing contact angle for TEO₄ in the course of spreading on PP, PF and TF substrate at 22 °C (a) and at 5 °C (b). Note that we did not study phase behaviour of those solutions. However, even a visual inspection showed that all solutions at low temperatures were cloudy. As expected the aqueous solutions of TEO₄ improve its wetting performance at Tᵢ = 5 ± 2 °C on all surfaces, and on PP it shows complete wetting. Solutions of TEO₆

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**Fig. 5.** Final contact angles for droplets of aqueous solutions of trisiloxane surfactants vs. concentration on different polymer substrates at room temperature: (a) Teflon AF, vertical straight line shows a point of inflection corresponding to 1 CWC, a dashed area shows a range of 1 CAC values for all trisiloxanes studied; (b) polypropylene, Parafilm, a dashed line corresponds to a final zero contact angle.

**Fig. 6.** (a–b) Final contact angles vs. number of ethylene oxide units (EO) of trisiloxane surfactants on TF (●), PF (■), and PP (♦), at room temperature: (a) CAC and (b) CWC.

**Fig. 7.** (a–b) Time evolution of advancing contact angles of TEO₄ at room temperature (a) and at low temperature (b) on polypropylene, Parafilm and Teflon AF surfaces.
showed complete wetting on moderately hydrophobic surfaces at both low and room temperatures as expected in accordance with observations in [23]. However, in the case of TEO₉ solutions spreading at these temperatures was different. At room temperature TEO₉ shows superspreading (complete wetting) on PP, and at low temperature wetting is considerable on PP substrate, but it still is a partial wetting with the final contact angle around 10°, Fig. 8.

3.3.2. Alkyl polyethylene ether surfactants

The CP temperature for polyoxyethylene alkyl ether surfactants increases with increasing the length of EO chain [24,25]. According to the literature data the CP for C₁₀EO₆ is close to the room temperature 20 °C [7,24], but increasing the length of EO chain by only two EO units leads to drastically increase of the CP: for C₁₀EO₈ the CP temperature rises to 60 °C [7,24] and above 60 °C [25]. Below we assume that the spreading capability of C₁₀EO₆ surfactants can be improved by reaching the CP temperature of their micellar solutions or, vice versa, similarly to the case of trisiloxanes, the spreading capability of C₁₀EO₆ surfactants is suppressed when temperature of solutions is lower the CP temperature. To the best of our knowledge no results on spreading characteristics of these surfactants have been reported previously in the literature. In Fig. 9 spreading kinetics of the micellar aqueous solution of C₁₀EO₆ at 75 ± 5 °C (that is above the CP) is compared with spreading of this solution at 22 °C (a few times below its CP) on polypropylene surfaces. It was observed that solution of C₁₀EO₆ became cloudy (by visual inspection) at temperature starting at 70 °C. Unfortunately strong evaporation and condensation did not make possible to observe the evolution of contact angle of a droplet for a prolonged period of time (longer than ~60 s). However, it was possible to compare the contact angles decrease caused by spreading over first 10–15 s when evaporation was ~10% at that high temperature. Experimental data presented in Fig. 9 clearly confirms that the aqueous solution in the two-phase (turbid) state shows faster spreading with lower the advancing contact angle as compared with the identical C₁₀EO₆ solution at room temperature. Fig. 10 shows a comparison of the evolutions of advancing contact angles of solution of C₁₀EO₄ at 5 °C (below the CP temperature) and the same solution at 22 °C (close to the CP temperature). As it was expected the spreading capability of this solution degrades with a decrease of temperature a few times below its cloud point.

4. Conclusions

Comparative study of spreading performance of aqueous solutions of trisiloxane surfactants with 4–9 ethylene oxide (EO) units and polyoxyethylene alkyl ethers with 10 hydrocarbon groups, and 3–8 EO units on polypropylene, Parafilm and Teflon AF in a wide range of concentrations and at different temperatures has been carried out.

It was shown, that both kinds of surfactants demonstrate three mode of spreading at room temperature depending on the concentration surfactants and the substrate used: (i) non-wetting when both an initial (θ₀) and a quasi-equilibrium final contact angle (θ∞) were above 90°; (ii) transition from non-wetting (θ₀ ≥ 90°) to partial wetting (θ∞ < 90°), and (iii) partial wetting (θ₀ < 90° and θ∞ < 90°). In the case of trisiloxanes with n(EO) = 5–9 at C ≥ CMC (critical wetting concentration) an extra mode (iv) – transition from partial wetting to complete wetting (superspreading) on polypropylene surface takes place.

Influence of the length of EO chains on wetting ability has a completely different character for C₁₀EO₆ and TEO₉. In the case of C₁₀EO₆ surfactants the final contact angle increases on all polymers with increasing number of EO units. Contrary to C₁₀EO₆ surfactants the final contact angles for TEO₉ solutions decrease with increasing of n(EO) reaching a minimum values at n(EO)=6–8 at CAC, and show complete spreading (θ∞ = 0) for n(EO) ≥ 6–8 at CWC on polypropylene and Parafilm at room temperature. Spreading capability of both kinds of surfactants depends strongly on temperature. According to the literature if trisiloxane solutions are kept at a temperature close to a cloud point (CP) when two immiscible
liquid–liquid phases appear and then superspreading is expected. It has been found that trisiloxane TEO₄, which is not a superspreader at room temperature (22 °C) exhibits superspreading at 5 °C, which is close to the CP, whereas TEO₅ solution, which is superspreader at 22 °C, becomes worse spreader at 5 °C. The same approach has been extended to polyoxyethylene alkyl ether surfactants: spreading capability of these surfactants can be tuned by changing temperature similar to that of trisiloxanes. This suggestion was confirmed for C₁₀EO₄ solutions (the CP at near 20 °C) and for C₁₅EO₅ solutions (the CP at above 60 °C). Experiments for micellar solutions of those surfactants on polypropylene results in the that θₙ of C₁₀EO₄ droplets increase at 5 °C (far from the CP) compared to 22 °C. In the case of droplets of C₁₅EO₅ its spreading capability has been improved: the θₙ decreases at 75 °C as compared with the room temperature.

Trisiloxanes show complete wetting on moderately hydrophobic polymers, but polyoxyethylene alkyl ethers do not show at all. Despite of that difference in spreading performance of trisiloxanes and polyoxyethylene alkyl ethers there is a common feature for both surfactants. The latter is a temperature-dependent spreading capability, which is due to non-ionic EO groups attached to the different hydrophobic tails. Spreading of both surfactants can be remarkably improved by the presence of dispersed phase in solutions at their cloud point temperature.

Acknowledgement

This research was supported by MULTYFLOW project (EU), EPSRC (UK) and PASTA project (European Space Agency).

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