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Wettability of paraffin surfaces by nonionic surfactants: Evaluation of surface roughness and nonylphenol ethoxylation degree

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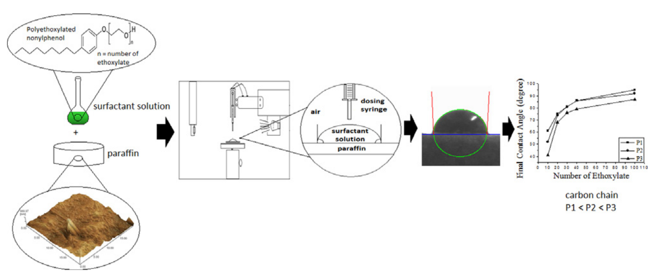
HIGHLIGHTS

- We investigate the wetting of three paraffin surfaces by surfactant solutions.
- We evaluated five surfactants with different ethoxylation degree.
- The sessile drop technique was employed.
- The surface morphology was the most important factor governing wetting properties.
- An increase in ethoxylation degree promotes a decline in paraffin wettability.

GRAPHICAL ABSTRACT



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ABSTRACT

Wettability is a widely used property in many industrial applications. This study aimed at determining the wettability of long-chain paraffin surfaces by nonionic surfactants, nonylphenol polyethoxylates with different ethoxylation degrees. Interactions between solid and liquid phases were determined by apparent contact angle measurements. The morphology was obtained by atomic force microscopy. The results demonstrated that the molar mass of paraffin has a direct influence on the wettability of the surfaces by surfactant solutions. The rise in paraffin molar mass promoted a reduction of the contact angle between solid–liquid interfaces due to the formation of surfaces with less roughness. An increase in the ethoxylation degree of surfactants reduced the wettability, showing a tendency toward water behavior. It was observed that the melted paraffin crystallized more abruptly due to having a higher melting temperature, which impedes crystal formation and, consequently, decreases its roughness.

1. Introduction

Wettability is the tendency of a liquid to spread out over a solid surface. In wetting processes it is important to evaluate the level of spreading and the rate of wetting. According to Darmanin and Guittard [1], the wetting process is governed by three main parameters: the liquid-repellent properties of the compounds present at the extreme surface, the surface roughness, and the surface morphology or topography. The control or modification of wettability can be applied in different fields, such as: agricultural products [2]; dental implants [3,4]; coating materials and adhesives [5]; and petroleum production [6,7]. One of the ways to alter the wettability of solid substrates is using surfactants.

Surfactants are amphiphilic molecules with an affinity for both polar and nonpolar media. It is well known that surfactants in aqueous solutions exhibit two important characteristics: one is related to their capacity to cluster into micelles and the other is the ability to adsorb at the interface. The critical micelle concentration (c.m.c.)

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is the concentration of surfactants in which micelles start to form [8].

Different techniques are used to determine the wettability. The most widely used technique is the measurement of the contact angle [9,10]. As the Young contact angle is an unmeasurable physical value [11], the Young equation [11,12] can be used to obtain the equilibrium contact angle between the solid/liquid/gas phases (three phase contact line), see the following equation.

$$\cos\theta_0 = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where γ_{SV}, γ_{SL}, and γ_{LV} represent the interfacial tensions at the boundaries between liquid (L), solid (S), and vapor (V) and θ_0 is the Young contact angle. This method allows one to obtain the adhesive-cohesive relationship between two fluids, liquid–vapor or liquid–liquid, using internal angles in contact with the solid surface. When the value of θ_0 is less than 90°, the liquid wets the solid and when it is higher than 90°, the liquid is non-wetting. Values of θ_0 equal to 0° and equal to 180° indicate the conditions of complete wetting and complete non-wetting, respectively.

The most frequently used method to determine the contact angle is the sessile drop [13–15]. This method allows observing small variations in the behavior of a liquid drop deposited on a solid surface. Among the methods used to determine the contact angle, those which use the principle established by the Young equation, where the equilibrium between surface and interface tensions help in wettability, should be highlighted [16–21].

Another method used to describe the wettable behavior of a surface takes into account the determination of the hysteresis contact angle existing in processes involving solid and liquid phases, which is obtained by measurements of advancing and receding contact angles [22,23]. Different factors, such as drop size [24], operator error, surface roughness and heterogeneity [25,26], contaminated fluids, and sample geometry can influence the measurement of the contact angle [15,27].

The wetting of a solid by a liquid is considered interesting not only from a theoretical aspect but also considering practical applications. Surface wetting is associated with corrosiveness, lubricity, and adherence which are of great interest of several industries. Paraffin is a petroleum-based alkane mixture whose surface is strongly hydrophobic. As such, it has been used in a number of wetting studies [21,28–30]. It is well known that the addition of surfactants to water enhances the ability of aqueous solutions to wet solid surfaces.

The present study aimed at determining the wettability of three different paraffin surfaces by aqueous solutions of surfactants (nonylphenol polyethoxylates). The results of the evolution of the advancing contact angle, establishing a relationship between dynamic wetting with spreading over time were reported. The influence of the surfactant ethoxylation degree was evaluated, using solutions at different concentrations, according to each surfactant's critical micelle concentration. In addition, the effect of the hydrophilic–lipophilic balance of the surfactants on the wettability of the paraffin surfaces used was assessed. Finally, the ultimate objective was to develop new knowledge of paraffin wettability by nonionic surfactant solutions.

2. Materials and methods

2.1. Materials

The nonylphenol polyethoxylate surfactants used in the tests were of commercial grade and employed with no prior purification. Their references are NP10EO, NP20EO, NP30EO, NP40EO, and NP100EO, with NP representing nonylphenol and nEO the average number of ethylene oxide units present in the surfactant molecule.

Table 1
Surfactants used and their characteristics.

Surfactant	Molar mass (g/mol)	HLB[a]
NP10EO	661	13.3
NP20EO	1100	16.4
NP30EO	1540	17.1
NP40EO	1980	17.8
NP100EO	4620	19.0

[a] HLB, hydrophilic–lipophilic balance.

Table 1 shows some of the characteristics of the nonionic surfactants used.

The surfactant solutions were prepared using distilled water. Contact angle and surface tension were measured with recently prepared solutions to avoid any mass loss by evaporation or contamination.

The three paraffin materials, kindly supplied by Petrobras, were used as received. Their melting temperatures were measured using a digital melting point apparatus (Microquimica, MQAPF-302). The paraffinic substrates were obtained by heating each of the paraffin materials until reaching their melting point and depositing them in a PVC molding apparatus (3.0 cm inner diameter and 1.5 cm height). Samples were approximately 1.0 cm thick. The PVC molding apparatus had a polished stainless steel plate in the base to minimize imperfections during crystallization of the surfaces.

2.2. Methods

2.2.1. Contact angle

All the apparent contact angles (θ_{ap}), defined as the angle between the apparent solid surface and the tangent to the liquid–fluid interface [31,32], were measured using a goniometer (Krüss, DSA 100). Drops (5 μL) were automatically deposited on the paraffin's surface using a microsyringe (0.5 mm-diameter capillary tip) installed in the device. The measurements were monitored by using a high-resolution camera installed in the apparatus (25 pictures per second). An LED diffuser with a white background was used as light source. A screen was placed between the light source and the drop to minimize heating and provide uniform lighting and good contrast without mass loss during deposition. The images of each drop were monitored using a software, from the beginning to the end of the experiment, and the same software was used to record the images. The experiment started at the moment the drop was deposited on the surface and lasted 60 s. The software calculated the apparent contact angles instantaneously, producing a sheet of contact angle as a function of time. Equilibrium contact angles were achieved under these experimental conditions.

2.2.2. Critical micelle concentration (c.m.c.)

Surface tension measurements were used to determine the c.m.c. of each surfactant under consideration. The same goniometer (Krüss, DSA 100) was used to obtain surface tension values applying the pendant drop technique [5,33]. The goniometer was operated using a software that allowed automatic measurement and real-time calculation of the surface tension using the Young-Laplace equation. All the experiments were made at room temperature (25 °C).

2.2.3. Assessment of excess surfactant at the interface

The study of surfactant adsorption at liquid interfaces is based on the Gibbs adsorption equation [34–36]. It shows the extent of adsorption on a liquid surface, determined from surface tension data. Thus, it is possible to estimate surfactant adsorption at the