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Wettability Study of Super-Hydrophobic Silica Aerogel Powders

F. Raoufi[1], Z. Ranjbar[1, 2]*, S. Rategar[3], E. Nowak[4], B. Nazari[1]

1. Faculty of Surface Coating and Novel Technologies, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran
2. Center of Excellence for Color Science and Technology, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran
3. Radsys Pooshesh Knowledge based Co., P.O. Box: 16765654, Tehran- Iran
4. College of Sciences, Massey University, P.O. Box: 756, Auckland, New Zealand

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ABSTRACT

Due to the importance of super-hydrophobic silica aerogel powder as a material in the field of energy saving, its wettability in the presence of various surfactants was investigated. One anionic and two non-ionic surfactants with different molecular structures were used as wetting and dispersing agents. Wetting properties of the aerogel powders were investigated by the contact angle measurements based on sessile drop method. The experimental results demonstrated that the silica aerogel powders are highly hydrophobic which is attributed to their surface treatment with the agents containing organic end groups. Moreover, it was found that anionic surfactant (Sulfosuccinate) was more efficient than non-ionic surfactants (Alkyl EO/PO copolymer and OctylphenolEthoxylate) in reducing the contact angle of water on silica aerogel powders. Further, the sessile drop method with slide and adhesive gave consistent data with good reproducibility for the investigated powders. Prog. Color Colorants Coat. 13 (2020), 75-83© Institute for Color Science and Technology.

1. Introduction

Silica aerogel is a highly porous solid material derived from a silica gel in which the liquid component is replaced by air. In recent years, silica aerogels have attracted increasingly more attention due to their extraordinary properties. These materials are nanostructured non-crystalline solids with a number of excellent physicochemical properties such as low density, high porosity, high surface area, low thermal conductivity and adjustable surface chemistry [1-4].

These properties make silica aerogels unique and promising in a number of applications. Thermal insulation is the obvious one due to the low thermal conductivity, i.e. 0.012 W/m^2K, compared to typically used polystyrene 0.033 or glass wool 0.023, leading to enormous financial savings [5, 6]. In fact, low thermal conductivity of silica aerogels is attributed to the nano-porous structure which is filled with still air as the size of pores is smaller than the mean free path of bulk air [7]. Silica aerogels are available with different morphologies, e.g. monoliths, granules or powders. Monolithic silica aerogels are well suited to the energy savings mostly in the form of transparent and super insulating double windows [8, 9]. Silica aerogels in the form of powder and granule have been used as additives in thermal insulation coatings and concretes, respectively [10-12].

Wettability of fine powders and agglomerates is an essential feature in a number of practical applications and processes such as dissolution, dispersion, granulation, coating, drying, etc. [13]. To be used in the water borne thermal insulation coatings, silica aerogel particles need to be dispersed in the aqueous medium. Therefore, their wettability plays a key role in

*Corresponding author: ranjbar@icrc.ac.ir

the process, as wetting is the first step of the dispersion. Wetting can be described as the interaction between the solid and liquid which relies on the concept of contact angle. Contact angle is a physicochemical property of any given system and depends on the interfacial energies of the solid–liquid, liquid–vapor and solid–vapor interfaces and is formulated by the well-known Young's equation (Eq. 1) [14].

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cdot \cos\theta \qquad (1)$$

Where γ_{sl}, $\gamma_{sv}, and\, \gamma_{lv}$ are solid-liquid, solid-vapor, and liquid-vapor interfacial tensions, respectively. The contact angle is a useful and concise indicator of hydrophobicity/ hydrophilicity of the solids. That is, the lower the contact angle, the higher is the wettability of the surface. Experimental methods for wettability assessment of powders have been reviewed [15]. Among them, sessile drop method is widely used mostly because of its simplicity and availability.

Hydrophobic powders are not wettable and cannot dispersed uniformly in aqueous medium solely by mechanical mixing, and appropriate type and amount of dispersing/wetting agents are needed for fine and homogenous dispersion [16]. Wetting agents are commonly surfactants that lower the surface tension of a substance. This allows the liquid to spread more easily across any solid surface [17]. A small amount of surfactant on the surface or in the test liquid could potentially change the wettability in practical applications. There are four main types of wetting agents: anionic, cationic, amphoteric, and nonionic. The interaction between the dispersant and the particle is of major importance, and its optimization permits to ensure a good quality of the dispersion. Effects of different types of surfactants on wetting properties of hydrophobic surfaces and powders have been widely studied [13, 16, 18-21]. Although several studies have been done regarding the alteration of silica aerogel hydrophobicity, all of them focus on the chemical surface treatment of the solid [22-24].

The aim of the present study is to investigate the effect of surfactants on the wetting properties of highly hydrophobic silica aerogel powder in aqueous medium to assess their efficiency as dispersant in insulating coatings. The wetting properties of the powders are not studied to a great extent in the literature. In this study, the effect of ionic and non-ionic surfactants on the wettability of highly hydrophobic silica aerogel powder is studied in a wide range of concentrations. The contact angles of pure water and surfactant solutions have been measured by the sessile drop method.

2. Experimental

2.1. Materials

Two different grades of silica aerogel powder, Enova IC3100 and EnovaIC3110 (CABOT, USA), were used as received to study the wettability. Size and morphology of the silica aerogels have been determined by scanning electron microscopy (SEM, LEO 1455VP) (Figure 1). Fourier transform infrared spectroscopy (ATR- FTIR, Thermo Nicolet Smart Golden Gate MKII single reflection ATR spectrometer, 4000 to 400 cm^{-1}) was performed in order to characterize the functional groups of the aerogel surfaces. The resulted spectra are shown in Figure 2. Surface area, pore volume, and average pore size of the powders were measured by Nitrogen sorption analysis. The physical properties of the aerogels are summarized in Table 1.

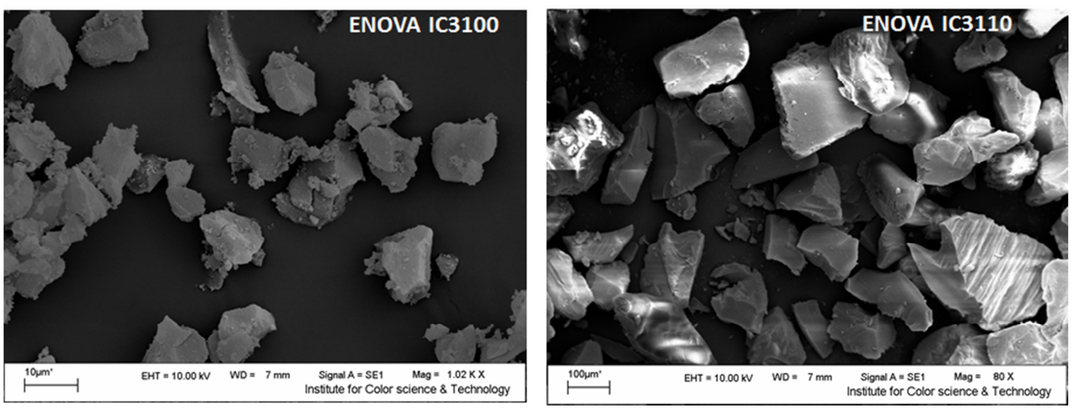

Figure 1: SEM images of silica aerogels.

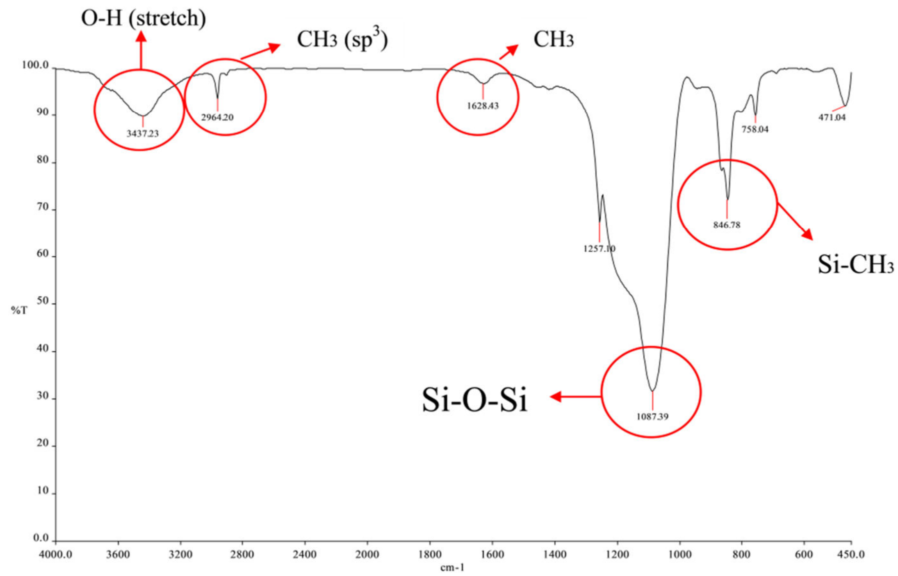

Figure 2: FT-IR spectrum of silica aerogels.

Table 1: Properties of the silica aerogel powders.

Title	IC3100	IC3110
Particle size (μm)[1]	20-40	100-700
Surface area (m^2/g)[2]	733	736
Pore volume (ml/g)[2]	2.40	2.77
Average Pore size (nm)[2]	13.1	15.1
Bulk density (kg/m^3)[3]	120-150	120-150
Water affinity	Hydrophobic	Hydrophobic
Thermal conductivity (W/m.K)[3]	0.012	0.012

[1] According to the SEM images
[2] Brunauer–Emmett Teller (BET) method
[3] TDS from the manufacturer

Three different surfactants with different properties (one anionic and two nonionic) were used to examine the effect of surfactants on wetting of super-hydrophobic silica aerogel surfaces. The anionic surfactant was sodium sulfosuccinate ester (TRITON™ GR-5M). An alkyl EO/PO copolymer (TERGITOL™ XD) and an octylphenol ethoxylate surfactant (TRITON™ X-100) were used as nonionic surfactants. All the surfactants were obtained from DOW Chemical, USA. The molecular structure of the surfactants is shown in Figure 3. Distilled and deionized water with conductivity of <10 μS/cm were used in the experiments.

2.2. Methods

2.2.1. Sessile drop method

Although the sessile drop method is generally applied for smooth, flat and nonporous surfaces, this technique is one of the most common methods used to determine the wettability of powders. It is a direct and simple way to measure the contact angle of a liquid droplet on a solid surface just by using a camera and image analysis tool (e.g. ImageJ, NIH). There are two procedures to perform this technique for powder samples. The first one is to compress the powder into a disc/pellet by applying a high pressure (~70–700 MPa) and then

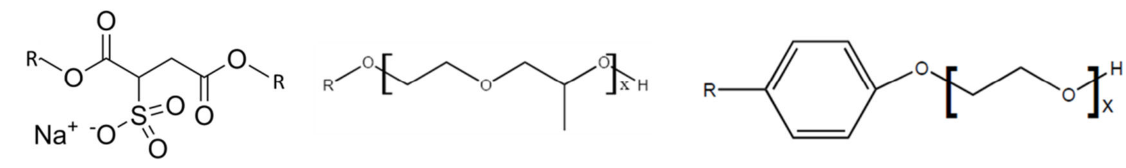

Figure 3: Molecular structures of the investigated surfactants.

measuring the contact angle of the liquid of interest; however, the adsorption of liquid into the disc/pellet makes the reading uncertain. The alternative procedure is based on attaching a thin layer of the particles on a substrate with the aid of an adhesive and then measuring the contact angle [14].

In this study, particles were placed on the surface of glass microscope slides (60×25×1.5 mm) which were covered with double sided adhesive tape. After 30 s, particles not firmly attached to the surface were removed. A 10 μL droplet of water or aqueous surfactant solutions were placed on the slide and the images of the drop were captured every 1 s for a total period of 60 s. contact angles were calculated by analyzing the images. Each measurement was repeated at least three times and the average was reported.

3. Results and Discussion

3.1. Wettability of silica aerogels by water.

Before the measurement of contact angles between silica aerogel particles and water, it is essential to test the interaction between water and the adhesive tape used to attach the particles. The measured contact angle between the glass slide covered with double sided adhesive tape and water was about 85°. Then, the contact angle between the water droplet and the glass covered with aerogels IC3100 and IC3100 were measured, which were almost identical and equal to 145° (Figure 4).

The difference between the contact angle of the water droplet on the powders and that on the tape clearly indicates that the coverage of the slide surface with powders was very good and the wettability of powders has been truly assessed [14]. Also, the reproducibility of measurements was very good and the standard deviations, based on the three individual measurements, were less than 5°. The shape and size of the water droplet placed on the slide did not vary significantly with the measurement time, indicating that all forces acting on the droplet were in equilibrium. The results also showed that the static contact angles between water and the particles bed have been quantified. Also, the equality of water droplet's contact angles on both aerogel powders, i.e. IC3100 and IC3110, with different particle size distributions suggests that the size of the particles does not have any effect on the contact angle determined by this method.

(a)

(b)

(c)

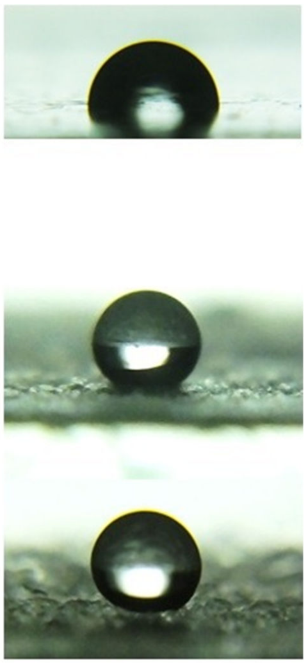

Figure 4: Droplet of water placed on the glass slides covered with (a) adhesive tape, (b) silica aerogel IC3100, and (c) silica aerogel IC3110.

The high hydrophobicity of particles is attributed to their surface treatment by the manufacturer. Silica aerogels synthesized with tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) are inherently hydrophilic due to the presence of surface active hydroxyl (–OH) end groups. This can be overcome by modifying the aerogel surface, replacing the –OH group with the hydrophobic organic functional group, O–Si–$(CH_3)_3$ [1]. The use of agents with organic end groups, such as trimethylchlorosilane (TMCS), hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDZ), or methyltriethoxy-silane (MTES) leads to the replacement of –OH with hydrophobic groups. According to the MSDS, which confirmed by the FT-IR analysis, Cabot silica aerogel powders are silylated with trimethylsilyloxysilane to become highly hydrophobic that leads to water contact angle of 145°. Absorption peak of -C-H (aliphatic) stretching in the range of 2900-3000 cm^{-1} indicates successful capping of the silica surface with methyl groups Figure 2.

These findings can also be explained by the Young's equation (Eq. 1), which relates the balance between the adhesive forces between a liquid and solid that cause a liquid drop to spread across the surface, γ_{sl}, and the cohesive forces within the liquid and solid that cause the drop to ball up and avoid contact with the surface, γ_{sv}, and γ_{lv} For any solid, Cosθ increases with decreasing the surface tension (γ_{lv}) of the liquid. The intercept when Cos θ = 1 is the critical surface tension (γ_c) of that surface. This critical surface tension is an important parameter because it is a characteristic of the solid and determines the wettability of the surface. In other words, solid surfaces are divided into high-energy and low-energy surfaces. Most liquids achieve complete wetting with high-energy surfaces which is not the case for low-energy surfaces. That is, the higher the energy of a solid, the better is the wetting. This energy is determined by the outermost chemical groups of the solid. In the case of silica aerogel powders, replacing the –OH group with the hydrophobic organic functional group, O–Si–$(CH_3)_3$, reduces the energy of the solid surface, which leads to its high hydrophobicity according to Young's equation.

The sessile drop is a simple and reproducible method in which a powder layer is deposited on a substrate using an adhesive tape. Although there is no compacting pressure affecting the surface properties of the powder and no drop penetration and air trapping, surface roughness results in only the apparent contact angle, not the actual contact angle which derives from the Young's equation, the difference leads to the invoking of the models of roughness like Wenzel model and Cassie- Baxter model.

3.2. Wettability of silica aerogel by aqueous surfactant solutions

In this work, two nonionic surfactants (Alkyl EO/PO copolymer, octylphenolethoxylate) and one anionic surfactant (sodium sulfosuccinate ester) were considered as wetting agents. Three surfactant concentrations, i.e. 0.1, 1 and 5 wt%, were selected in contact angle tests to evaluate their wettability. It should be noted that all the selected surfactant concentrations are far above the critical micelle concentration (CMC) due to the intense hydrophobicity and high surface area of the silica aerogel particles. Low surfactant concentrations are not able to penetrate into the pores and displace air. The physical properties of the solutions are presented in Table 2.

Table 2: Properties of the surfactant solutions.

Surfactant	Concentration wt%	Surface tension mN/m	Viscosity mPa s
TERGITOL XD	0.1	35.0	1
	1	33.0	1.11
	5	32.4	2.17
TRITON X100	0.1	31.3	1
	1	30.3	1.08
	5	30.	1.88
TRITON GR5M	0.1	26.3	1.12
	1	25.7	2.35
	5	25.4	14.50

Figure 5 shows the variation of contact angle with time for the aqueous droplets containing different concentrations of different surfactants on glass slides covered by silica aerogel IC3100. Again, it is noticeable that the particle size does not have any meaningful effect on the contact angle between surfactant solutions and the aerogels. That is, the behavior of the drop on both powders can be considered identical; thus, the variation of contact angles on IC3110 is not depicted in this figure. In addition, the values are within the standard deviation of the measurement which is 5°. The variation of contact angle with surfactant type and concentration shows that the surfactants could decrease the contact angle of silica aerogel powder to various extents. The photographs of some aqueous droplets on the silica aerogel powders provide more direct observation in Figure 6.

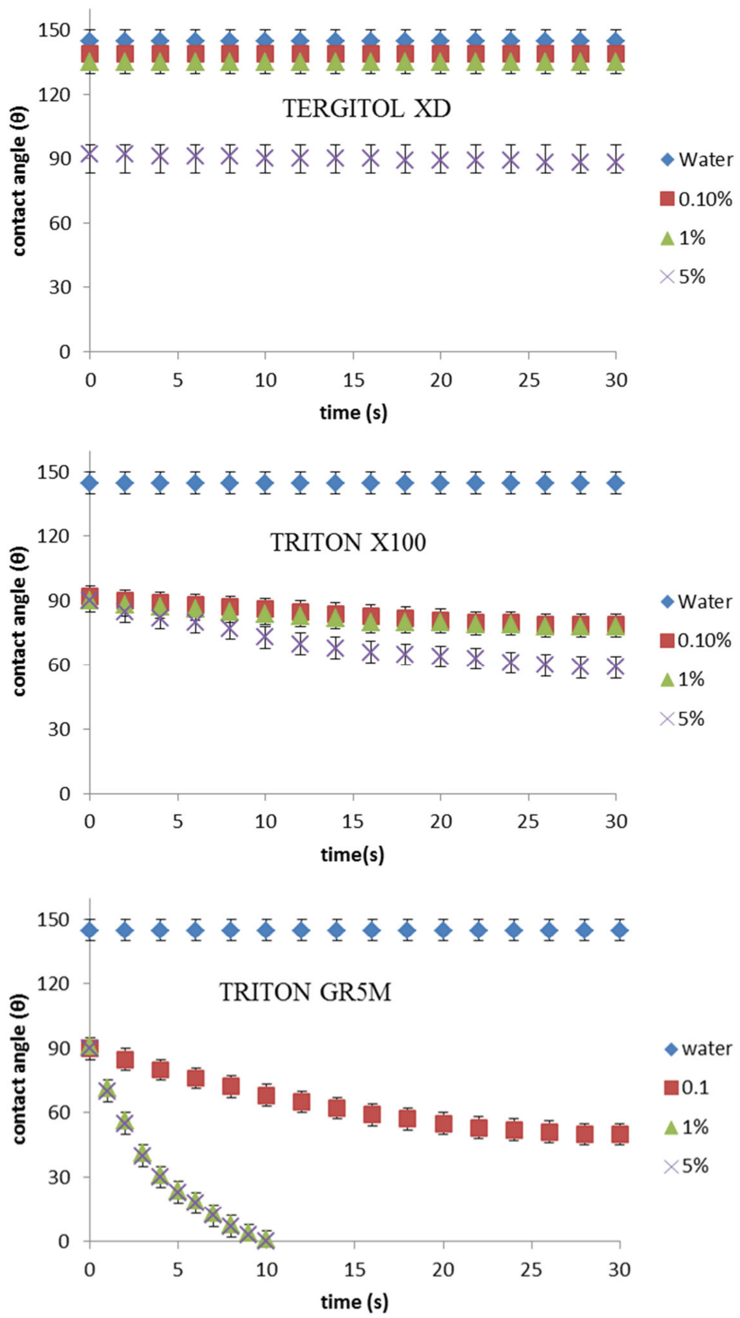

Figure 5: Contact angle between surfactant solutions and silica aerogel IC3100 measured by sessile drop method.

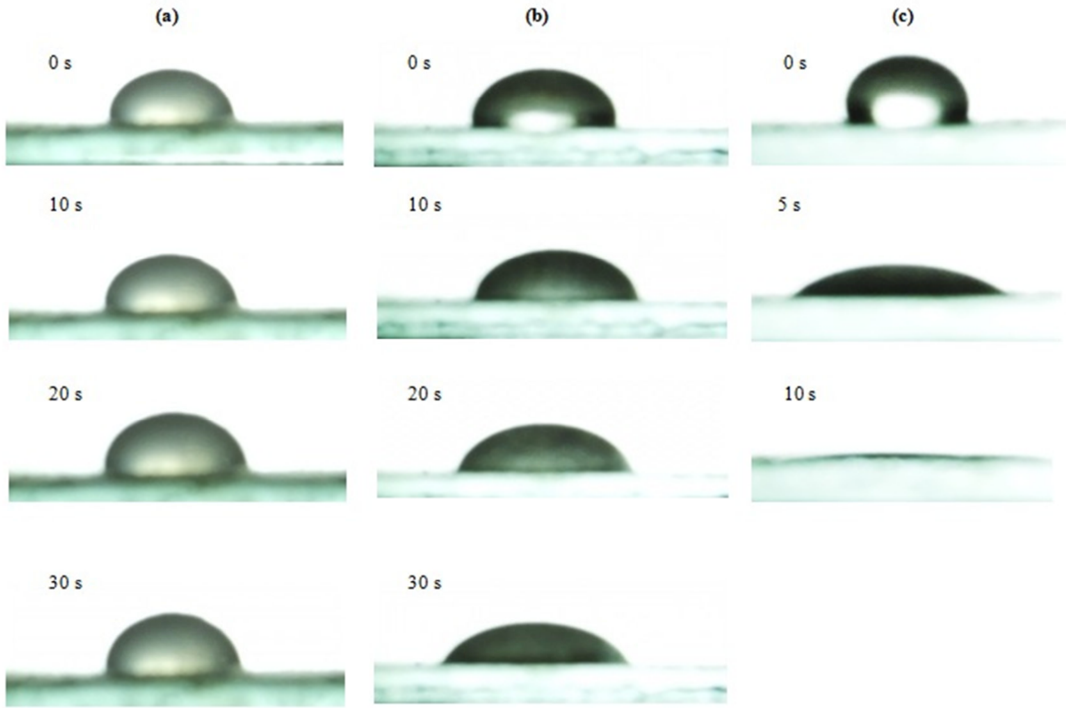

Figure 6: Droplets of 5 wt% surfactant solutions on silica aerogel IC3110 (a) Tergitol XD (b), Triton X100 and (c) Triton GR5M.

According to the surfactant type added, the behavior of contact angle can be divided into three different groups. For Alkyl EO/PO copolymer surfactant (TERGITOL™ XD), the contact angle reaches a constant value almost immediately when the aqueous droplet is settled on the powder. Also, shape and size of the droplet placed on the slide remain constant to some extent with time, which means that the forces applied to the droplet are balanced quickly and the contact angle is the static one. Although the decrease in the contact angle in comparison with the water droplet is noticeable, the extent of change is not so great. In other words, even at the highest level of surfactant concentration, i.e. 5%, the contact angle is about 90°, which means that the liquid poorly wets the powder. This can be attributed to the molecular structure of Alkyl EO/PO copolymer which is a macro molecule with a very high molecular weight. These types of surfactants are mostly used as stabilizer or dispersant in different industrial applications like agrochemicals or paints and coatings due to their excellent steric hindrance. Hence, they cannot be considered as good wetting agents.

For the octylphenolethoxylate (TRITON™ X-100), the effect of surfactant can be seen immediately as the initial angle between the droplet and aerogel powder right after the contact is reduced to 90°. However, the angle is not constant with time, and the droplet immediately starts to spread over the powders from the contact point. It takes about 30 seconds for the droplet to find its final shape and reaches equilibrium, as no changes were observed after about 60 seconds. The equilibrium contact angle for 5% TRITON™ X-100 aqueous solution is 60° on both aerogel powders and 80° for 0.1 and 1 % on both aerogels. TRITON™ X-100 has a hydrophilic polyethylene oxide chain (on average it has 9.5 ethylene oxide units) and an aromatic hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group. The wettability of TRITON™ X-100 is designated to the phenyl ring in the hydrophobic part of the surfactant which causes a mutual interaction between the hydrophobic particle and surfactant molecule and leads to the adsorption of surfactant.

TRITON™ X-100 is widely used in various industrial applications as an excellent detergent, dispersant and emulsifier for oil-in-water systems and a very good wetting agent.

For anionic surfactant of sodium sulfosuccinate ester (TRITON™ GR-5M) at concentrations of 1% and 5%, the angles fall rapidly to a quite small value (<3°) within 10 s, following which the angle becomes undermined due to experimental uncertainty but it is clear that the contact angle will reach 0° very fast as seen in Figure 5. Clearly, drops were not in equilibrium when they were spreading and there were forces acting on them. Therefore, the conditions defining contact angle, i.e. equilibrium between surface forces, were not fulfilled and the results obtained before the equilibrium do not represent the static contact angle. The results show that the sodium sulfosuccinate ester is the best one among the three investigated surfactants regarding its wetting power. In fact, these surfactants are the best known wetting agents. They are also foaming agents, dispersants and emulsifiers and used in emulsion polymerization and dispersion of pigments in paints and latex, shampoos, cosmetics, etc.

Since there are no reactive groups at the surface of the silica aerogels, there would be no possibility of chemical reaction between the surfactant and the particle surface. Therefore, the difference in the contact angles obtained for the three surfactants with different concentrations should only be attributed to the surface tensions of the aqueous solutions shown in the Table 2. In fact, the surface tensions of Alkyl EO/PO copolymer (TERGITOL XD) solutions are about 30% higher than that of Sodium Sulfosucinate ester (TRITON GR-5M) and about 10% higher than that of Octylphenol-Ethoxylate (TRITON X100) solutions. As a result, sodium sulfosuccinate ester is the best wetting agent among the three investigated surfactants followed by octylphenolethoxylate and then Alkyl EO/PO copolymer. The decrease of surface tensions by increasing the concentration of each surfactant is also noticeable in Table 2, which is also in accordance with the contact angle results.

4. Conclusions

In this work, the contact angle between silica aerogel particles and water was measured in the presence of ionic and non-ionic surfactants to assess the wettability of such highly porous powders. The sessile drop method on the powders attached to the slide by an adhesive tape was applied, and the detailed analysis of the results clearly indicated that the method provided consistent data with good reproducibility for the investigated powders. Moreover, among the three investigated surfactants, the anionic one based on sodium sulfosuccinate ester appeared to be the best wetting agent followed by the nonionic octylphenolehtoxilate. The nonionic alkyl EO/PO copolymer is not a great wetting agent.

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