Scale-resistant surfaces: Fundamental studies of the effect of surface energy on reducing scale formation

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ABSTRACT

In this work, we performed a systematic investigation of the effect of surface energy on scale formation. We made a catalogue of smooth substrates with varying surface energies by depositing self-assembled monolayers (SAMs) of functionalized coatings (organosilanes) on glass slides and exposed these substrates to a saturated aqueous solution of CaSO$_4$. The systems reached supersaturation due to evaporation of the aqueous phase over time, resulting in CaSO$_4$ scale formation on the substrates. We show a significant reduction in scale formation with decreasing surface energy. To determine the surface chemistry and elemental composition of the substrates, we characterized them by X-ray photoelectron spectroscopy, and the results of this study were used to explain the effect of chemistry on surface energy. Furthermore, by looking at the contribution of the substrates' surface energy from polar and apolar components, we demonstrate that the polar component is a key factor governing scale formation on a substrate. Hence, a significant reduction in scale deposition can be achieved by minimizing the polar sites at the surface-scale interface. The proposed approach is distinctive because it studies how changing the surface properties can result in scale mitigation, whereas previous research in the field mostly have focused on developing effective chemical inhibitors to change the solid and liquid properties in the fluid phase. Our findings provide a fundamental understanding of scale formation as a function of surface energy attributes and provide insights for the design of scale-resistant surfaces with potential for technological applications.

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1. Introduction

Scale formation is a major unresolved problem in numerous industries including water desalination and water treatment [1–3], power generation [4], oil and gas [5–7], and hydrometallurgy [8–11]. Scaling results in significant operational losses due to impaired heat transfer, flow blockage and increased pressure loss, under-deposit corrosion, and decreased equipment lifetime. The costs of heat exchanger fouling arising from cleaning, fluid treatment, additional hardware, and loss of energy and production have been estimated to be about 0.25% of the GDP (gross domestic product) of industrialized countries [4,12–14]. Considering the pervasiveness of the scaling problem, a significant body of research

has been devoted to finding techniques for scale mitigation over the past decades. These studies have mainly focused on developing effective chemical inhibitors [2,15,16] or on improving existing chemical/mechanical removal techniques [17,18]. These technologies, although promising, are generally expensive, energy intensive, environmentally unfriendly, and in most cases far from adequate in preventing scale formation [3,5,12,19–23]. Hence, alternative approaches for scale mitigation are of great interest.

The mechanism of scale formation can be described using the nucleation-growth theory [24–26]. According to the classical nucleation theory (CNT) [27,28], clusters of salt molecules that gather together under random thermal motion must reach a critical size to sustain growth. The free energy barrier (ΔG^*, J) for heterogeneous nucleation of a salt nucleus on a smooth substrate, and the corresponding nucleation rate (J, m^{-3} S^{-1}) are expressed as [24,29,30]:

$$\Delta G^* = \frac{\left(\pi \, \sigma_{\text{salt,solution}} \, r^{*2} \right) \left(2 - 3m + m^3 \right)}{3}$$

$$\text{where} \quad m = \frac{\left(\sigma_{\text{subs,solution}} - \sigma_{\text{subs,salt}} \right)}{\sigma_{\text{salt,solution}}} \tag{1}$$

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$$J = J_0 \exp \frac{-\Delta G^*}{kT} \quad (2)$$

where $\sigma_{salt,solution}$ (J/m^2) is the salt-solution interfacial energy, r^* (m) is the critical radius of scale nuclei, and the parameter m is the ratio of the interfacial energies, where $\sigma_{subs,salt}$ and $\sigma_{subs,solution}$ (J/m^2) are the substrate-salt nucleolus and substrate-solution interfacial energies, respectively. J_0 (m^{-3} S^{-1}) is a kinetic constant, and k (J/K) is the Bolzmann constant. According to CNT (and Eq. (1)), the smaller the affinity between the salt nucleus and the substrate (i.e., $\sigma_{subs,salt}$) in the crystallizing medium, the smaller m and the larger the free energy barrier (ΔG^*) for heterogeneous nucleation [26].

Hence, an alternate approach to scale mitigation includes lowering the substrate surface energy (that would result in a smaller $\sigma_{subs,salt}$), using functionalized coatings and surface treatments that inhibit scale formation [1,14,31–36]. While these studies are promising, they deal with specific surface treatments such as composite metallic–polymeric coatings [1,14], ion implantation, modifying surface roughness and surface energy of heat transfer surfaces [33], and sputtered coatings of diamond-like-carbon and TaC [32]. As a result, the effect of surface chemistry and interfacial interactions on scale inhibition is not easily quantifiable, and the physical mechanisms governing the phenomena remain largely unclear. Here, we systematically study the effect of surface energy in terms of the apolar (Lifshitz–van der Waals) and polar (Lewis acid and Lewis base) interactions on scale formation. Specifically, we show that the polar component has a significant effect and controls scale formation and provide insights for the design of scale-resistant surfaces.

From Eq. (1), it is clear that surface energy plays an important role in the nucleation of scale crystals on a substrate. To systematically study this effect, we made a catalogue of smooth substrates comprising functionalized coatings with various surface energies, by depositing self-assembled monolayers (SAMs) of organosilanes on glass slides. The goal of this research was to study the effect of surface energy on scale formation. So we needed to have a range of various surface energies. We chose this class of materials; because they provide a systematic range of surface energies, so they enabled our research goal. We characterized their surface energy by measuring contact angles of three probe fluids (water, ethylene glycol, diiodomethane) and quantifying the polar and apolar components of surface energy using the Van Oss–Good–Chaudhury approach [37,38]. We then exposed the modified surfaces to a solution of calcium sulfate in water at ~40 °C for 72 h. The starting solution was saturated with the salt, containing ~2 g/l CaSO$_4$. Over time, it became supersaturated due to the evaporation of the aqueous phase, and CaSO$_4$ scale deposits were formed on the test substrates. We measured the weight of the substrates before and after each run and observed a significant reduction in scale formation by reducing surface energy. We also characterized the withdrawn test substrates using scanning electron microscopy (SEM) and showed that scale formation becomes less with decreasing surface energy.

2. Experimental

2.1. Materials

Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (97%), trichloro (octadecyl)silane (≥90%), isobutyl(trimethoxy)silane (≥98%), trichloro(hexyl)silane (97%), 1,2-dichloro-tetramethyl-disilane (95%), dichloro-dimethylsilane (≥98.5%), triethoxy-phenylsilane (≥98.5%), trimethoxy-methylsilane (≥98%) were purchased from Sigma Aldrich. Calcium sulfate dehydrate (99.4%) was purchased from J.T. Baker and dissolved directly in deionized water (18 MΩ cm, Millipore) to make the starting saturated solutions.

2.2. Coating of smooth substrates

We coated SAMs of alkylchlorosilanes (R$_n$—Si—Cl$_{4-n}$) and alkylalkoxysilanes (R$_n$—Si—(OR')$_{4-n}$) on glass slides (75 × 25 × 1 mm^3), using a technique reported previously [40] (see Fig. 1). These silanes require substrate surfaces to be hydroxylated for their formation. The driving force for the self-assembly is the in situ formation of polysiloxane, which is connected to surface silanol groups (—SiOH) via Si—O—Si bonds. SAMs of alkylchlorosilanes, with R$_n$—Si—Cl$_{4-n}$ precursor, were fabricated using a solution of 0.1 vol% silane in toluene; 0.6 vol% water was added to the solution to promote the reaction. Glass slides were immersed in the solution and sonicated for 2 min. After the reaction was completed, modified substrates were cleaned by sonication in acetone for 2 min and dried using N$_2$ gas (Air gas, NI300). Silane SAMs of alkylalkoxysilanes (R$_n$—Si—(OR')$_{4-n}$) were fabricated in an acidic environment to promote the reaction. Glass slides were immersed in a 0.2 vol% silane in ethanol under sonication for 2 min. Hydrochloric acid (from Mallinckrodt, ACS grade) was added to the solution to decrease the solution pH to 2 (~0.075 vol%). After sonication, glass slides were left in the silane solution for 24 h. They were then washed with water and dried with N$_2$ gas (Air gas, NI300).

2.3. Surface chemistry characterization (X-ray photoelectron spectroscopy)

To determine the surface chemistry and elemental composition of the substrates, we characterized them by X-ray photoelectron spectroscopy. XPS measurements were performed using a PHI 5600 ESCA multi-detection system with a base pressure of 1×10^{-10} torr. The X-ray radiation was the monochromatic Al $K\alpha$ line (1486.7 eV); the X-ray spot size and the takeoff angle were 0.8 mm and 45°, respectively. The survey spectra were recorded with a pass energy of 187.85 eV and an energy step of 0.8 eV. To obtain a good signal to noise ratio, at least four sweeps were performed for all surfaces. Data acquisition and processing were conducted using the AugerScan software (RBD Instruments, Inc.), and a Gaussian function for the fitting process. Before analyzing XPS data, the contribution of Al $K\alpha$ satellite lines was subtracted and the background was removed by a Shirley routine. For all measurements, spectral calibration was determined with respect to the C 1s at 285 eV. The surface compositions were obtained by normalizing the area under the curve using the manufacturer's sensitivity factors.

2.4. Contact angle measurements

Contact angles for the three probe liquids of diiodomethane (DIM, Alfa Aesar), ethylene glycol (EG, Alfa Aesar), and deionized water (18 MΩ cm, Millipore) were measured using a Ramé-Hart M500 advanced goniometer. Contact angles were taken as an average of at least 10 measurements. Drops of 5 μl at room temperature were deposited at a rate of 0.2 μl/s.

2.5. Experimental procedure

To systematically study the effect of surface energy on scale formation, we immersed four identical substrates inside a rectangular dish, with a dimension of 107 mm (L) × 87 mm (W) × 70 mm (H), using a multi-position glass slide rack. To reduce the surface energy of the dish and slides rack and to prevent preferential scale formation, we coated them with trichloro(1H,1H,2H,2H-perfluorooctyl)silane before the experiment. The rectangular dishes were filled with a saturated solution of CaSO$_4$ in water at 40 °C and placed on a multi-position hotplate (Ika Works IKAMAG RT 15 position Hot Plate) (see Fig. 2(a)). Temperature was set at 40 °C and held within ±3 °C of the set point. The experimental setup