The use of surfactants in the cleaning of works of art

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Abstract

Surfactants have been historically used for cleaning artifacts, but it was only in the last decades that serendipitous approaches were replaced by research in the field of soft matter and colloid science. Surfactants are components of nanostructured fluids, which were assessed for the removal of soil and aged coatings from paintings and are fundamental in processes that range from the inclusion of grime in micelles to the swelling and dewetting of polymer layers. Intriguing aspects involve the synthesis and use of biodegradable and self-cleavable surfactants, and the confinement of nanostructured fluids in gels, which boost the selectiveness of cleaning interventions. The performances of these advanced systems surpass those of traditional cleaning materials such as solvent blends and thickeners. The most important results are here reviewed and future perspectives given. Besides granting the transfer of cultural heritage to future generations, advanced cleaning materials are relevant to transversal fields, such as detergency, cosmetics, and drug delivery.

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Introduction

Cultural heritage is an ethical, societal, and financial resource; it promotes education and social inclusion and leads to economic benefits through tourism and job creation [1−4]. To produce such benefits, works of art must be well preserved and accessible; however, artifacts are subjected to degradation by soil, light, temperature, aqueous solutions, microorganisms, or detrimental products applied in wrong conservation interventions [5−7]. In a similar approach as medicine, with artifacts playing the role of "patients", science is central to both diagnostics [8−13], where the objects and their degradation are characterized, and "therapy", where actual materials and methodologies are applied to works of art to remedy and counteract degradation [14••−18•].

One of the main fields where science contributes to remedial conservation is the cleaning of works of art, i.e. the removal of unwanted layers that jeopardize the surface of the works. Cleaning is a crucial task, as it aims to restore the original aesthetic and ethical messages conveyed by the artifacts. Typically, the substances to be removed include dirt, soil, aged restoration products (glues, adhesives, or varnishes), or overpaints. The fundamental requirement is for the removal to be selective and non-invasive to the original components of the objects, which has historically rendered cleaning a delicate intervention. To add to the complexity of selectively removing layers from surfaces where numerous types of physical and chemical interactions are at play, conservation ethics introduced the debate on the so-called "patina", a layer of aged or corrosion products that can be granted aesthetic or historical value [19].

Coping with such practical and ethical issues, the removal of soil from artistic surfaces is an antique practice. Early restorers used, with a trial-and-error approach, a variety of natural materials including biological fluids (saliva, bile, and urine), food materials (wine, garlic, bread, and hot oil), ash, and simple soaps [18•,19]. Some of these materials already contained surfactants, enzymes, and chelators used in modern cleaning formulations. However, awareness of materials and methods used in art cleaning came slowly, whereas cleaning was already seen in the 17th century as potentially risky to the artifacts, it was in the 18th century that the profession of restorer emerged, posing questions on the effect of dirt and darkened varnishes [19]; nonetheless, cleaning methods have been specifically designed for the conservation of artifacts only since the late 1980s and the early 1990s [6,18•].

Traditionally, the removal of soil or other unwanted layers is carried out using the classic approach based on

organic solvents and polymer chemistry. Solubility parameters, such as those defined by Hildebrand [20] and later modified by Teas [21], are used to select specific solvent blends to swell or dissolve grime and aged varnishes (including natural or synthetic polymers). However, this approach involves significant issues. First, because the composition of original components in artifacts is often similar to that of unwanted layers, the use of free, nonconfined solvents is nonselective, with the risk of swelling and damaging underlying layers. Second, dissolved matter is quickly transported through the porous matrices of artifacts; grime and dissolved layers are thus "moved" deeper within the artifacts, rather than "removed" from their surface. Finally, solvents have toxicity issues, and in recent years, the use of green chemistry has been promoted in the field of cultural heritage conservation to decrease the impact of restoration materials on operators and the environment [22].

During the last decades, soft matter and colloid science have provided a new approach, where effective and safe cleaning materials have been developed, leading to a real revolution in the field [14••,23−28••]. In this context, the role of surfactants is crucial; they allow enhanced effectiveness and control of the cleaning process, overcoming the limitations of traditional solvent chemistry. For instance, nanostructured complex fluids, such as microemulsions and micellar solutions, can be formulated by the use of specific surfactants and solvents so as to remove unwanted layers through different physicochemical processes, ranging from classic detergency to selective swelling and detachment of layers or dewetting of polymer films, caused by the synergistic surfactant−solvent interaction [29•−32••].

In the following sections, we provide an overview of the most significant advancements in cleaning systems, where the use of surfactants is central. After describing the first aqueous systems featuring surfactants that were formulated for the removal of hydrophobic substances from hydrophilic surfaces, we will highlight recent applications of paramount importance in cleaning of art, i.e. the use of self-cleavable and biodegradable surfactants in nanostructured cleaning fluids, and the confinement of such fluids into retentive polymer matrices to allow controlled cleaning. Recent studies on the cleaning mechanisms of microemulsions will be discussed, taking advantage of relevant case studies where works of art were cleaned using advanced systems that outclassed traditional restoration materials. Finally, the use of water-in-oil microemulsions, "reversed microemulsions", will be discussed.

Surfactants in the traditional restoration practice

Classic detergency, using surfactants, is one of the main approaches for removal of hydrophobic unwanted layers

from artistic surfaces. For instance, greasy soil is commonly found on the surface of works of art, and it is easily targeted by aqueous solutions of surfactants. In binary water/soap systems, micelles (formed above the critical micelle concentration) are able to include hydrophobic, water-insoluble substances either in the hydrophobic core of the micelles, in the interfacial region, or in the micelles' peripheral hydrophilic region [29•]. The adsorption of surfactant molecules at the interface of water and hydrophobic substances contributes to the process, leading to the dispersion of such substances in the aqueous phase. Overall, detergency involves a complex set of mechanisms, comprising roll-up, emulsification, and solubilization (see Figure 1) [33•]. During roll-up, the surfactant solution wets the hydrophobic surface, and surfactants adsorb and wrap the hydrophobic substance into tiny droplets that are mechanically removed (see Figure 1a). Emulsification requires low interfacial tension between the hydrophobic surface and the surfactant solution; the detached oily droplets may stick to the substrate's surface. Solubilization often takes place with the dispersion of the oily soil into a microemulsion that forms *in situ* (Figure 1b), and the effectiveness of the process increases sharply when the temperature approaches the cloud point (for nonionic surfactant-based formulations); ultra-low interfacial tension between the oily soil and the surfactant solution is typically needed [6,29,33•].

Restorers have traditionally used natural materials containing surfactants to clean works of art. For instance, deoxycholic acid, found in bile, and abietic and aleuritic acids, found in natural resins, are surface active and able to solubilize specific materials found on the surface of artifacts, e.g. free fatty acids (from the degradation of oil paints) or di-terpenoids and tri-terpenoids (components of natural varnishes) [34•].

Wolbers reported on the use of aqueous surfactant solutions for the cleaning of painted surfaces in several publications starting from the end of the 1980s [18•,34•−37]. Topics such as the selection of surfactants, their combination with enzymes or chelators, and the thickening of the surfactants solutions with polymers to limit uncontrolled spreading on painted surfaces were treated. For instance, non-ionic surfactants were preferred for use in formulation with ionic materials commonly used in the cleaning of paintings, such as buffers and chelators [34•]. Non-ionic surfactants with a relatively low hydrophilic/lipophilic balance (HLB close to 12−17), such as Triton X-100, Brij 35, and Tween 20, were suggested for the cleaning of oil paints [34•,37]; in fact, because surfactants with higher HLB values have a stronger tendency to produce oil-in-water (o/w) emulsions, it was argued that their prolonged contact with oil paints would lead to swelling and dissolution of the original oil painted layers [34•]. Besides, the aforementioned nonionic surfactants all have

cloud points above room temperature, which prevents phase separation [34•]. When aqueous solutions at adjusted ionic strength are needed to clean surfaces, e.g. to limit the swelling of sensitive painted layers [34•,38], these nonionic surfactants are used in diluted ionic strength solutions, in the presence of monovalent ions (Na^+, K^+, NH_4^+) and ethanolate, rather than divalent ions (SO_3^{2-}, CO_3^{2-}), to avoid lowering the cloud point too much [37].

Surfactants are also commonly used to formulate o/w emulsions, where "oils" are water immiscible solvents dispersed as micron-sized droplets in the continuous aqueous phase. These systems are handy cleaning tools as they potentially combine the advantages of both aqueous and solvent chemistry and allow playing on factors such as pH, ionic strength, and solubility parameters to achieve good cleaning power. Some guidelines for the preparation of stable o/w emulsions for cleaning of paintings were provided by Wolbers and Stavroudis [18•], minimizing the water-solvent density difference [39]) and increasing the viscosity of the continuous aqueous phase with polymers such as cellulose ethers, polyacrylates, and gums (according to Stokes equation for creaming and sedimentation of dispersions, the rate of creaming of an emulsion is reduced if the droplet size and the density difference are both small and the viscosity high). However, the same authors recognize that the preparation of emulsions by restorers is typically a "by-hand" process, where the selection of surfactants is empirical. As a matter of fact, many conservators still prepare "in-house" cleaning

materials on a case-by-case basis [18•] and often through serendipity.

Cocoamine-based surfactants were used together with polyacrylic acid (PAA) in the so-called "solvent gels", introduced by Wolbers at the end of the 1980s to thicken both polar and nonpolar solvent solutions [36]. Namely, the commercial products Ethomeen® C12 and C25 are weakly basic nonionic cocoamine surfactants ethoxylated on the amino group (C25 has two hydrophilic chains, each with on average 7−8 oxyethylene units; C12 has two hydroxyethyl groups attached to the nitrogen atom), which are used to deprotonate the carboxylic groups in PAA; the polymer chains containing the deprotonated groups unfold to form an extended 3D network that thickens the solvent [34•,35]. The Ethomeen® molecules are bound to the PAA chains through ionic interactions, but they also act as weak nonionic surfactants to aid the cleaning action of the thickened solvents. Because Ethomeen® surfactants with different HLB are available, it is possible to prepare solvent gels either with low-polar (using Ethomeen C12®) or polar solvents (using Ethomeen C25®), which makes solvent gels extremely versatile.

However, while traditional surfactants, micellar solutions, and solvent gels can be versatile and effective tools, there are cleaning case studies where enhanced effectiveness and cleaning control are needed. Examples include the removal of aged polymeric consolidants that, owing to extensive cross-linking and chain scissions, exhibit decreased solubility in organic solvents

Figure 1
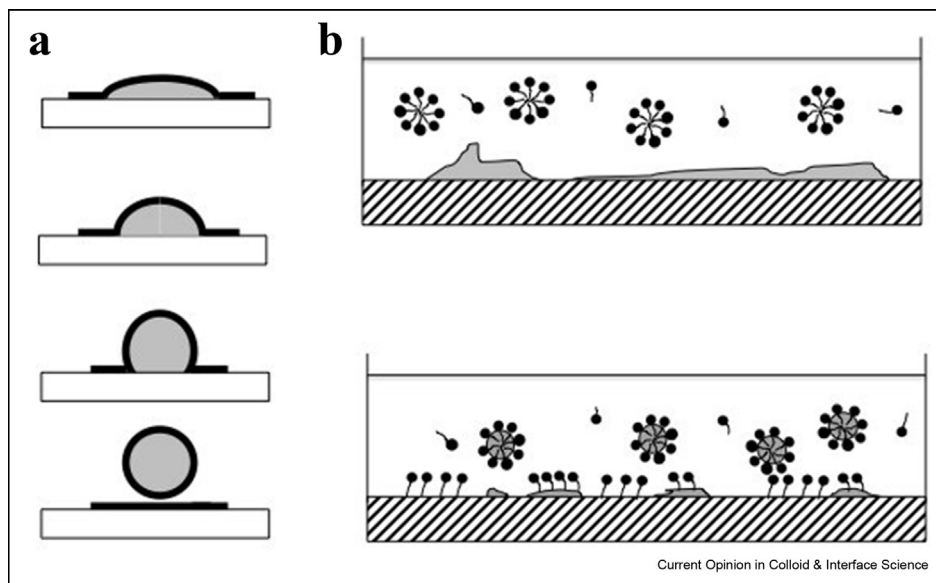
(a) Schematic illustration of the roll-up process. The white area represents the substrate surface, the grey region is the hydrophobic substance, and the thin black line is the layer of surfactant. **(b)** Schematic illustration of micellar solubilization. The hydrophobic substance (grey region) is solubilized in the inner hydrophobic pool of the micelles. Surfactant monomers also adsorb at the substrate and the oily surfaces. Adapted from Ref. 6 with permission from The Royal Society of Chemistry.

[40••] or the removal of adhesive tapes from solvent-sensitive paper artworks [26••]. Besides, the need to lower the environmental and toxicological impact of the cleaning fluids led to formulations where the solvent content is reduced to a minimum while maintaining high cleaning power, and to the introduction of biodegradable or self-cleavable surfactants. These advancements have been achieved in the last decades in the framework of colloid and nanosciences, and the main research highlights and applications are illustrated in the following sections.

Microemulsions

The cleaning effectiveness of emulsions can be enhanced dramatically when the size of the dispersed droplets passes from micron- to nano-size. In fact, the presence of nanosized droplets of solvent in the continuous phase can develop an interfacial area much larger than that of the same amount of bulk solvent, leading to a strong enhancement of the detergent power. In addition, the very dynamic nature of microemulsions as well as their thermodynamic stability are major assets in the cleaning process. Important parameters to form stable o/w or w/o microemulsions or bicontinuous phases were set by De Gennes and Taupin in 1982 [41•]. The authors proposed two main principles that must be satisfied for the formation of a microemulsion from a water + oil + surfactant system, avoiding the collapse of micelles into high-order structures such as lamellar and hexagonal phases: (a) the surfactant must be able to saturate the oil interface, without building pure (not swollen) micelles inside either the water or oil phase; (b) the interface must have a low rigidity (defined by the rigidity parameter K, which has dimensions of an energy), and the long–range interactions must be weak enough so that any "macrocrystal" formed can turn into less-organized structures.

The value of K can be modified by adding co-surfactants that increase the disorder of the interfacial film, a concept already present in the pioneering work by Schulman [42]. Controlling K means controlling the persistence length (ξ_k) of the interface, which can be defined as follows: the interface is flat at scales smaller than ξ_k, and consecutive portions of the interface with an area ξ_k^2 have independent orientations. The persistence length increases exponentially with the interface rigidity, following the equation $\xi_k = a \exp[2\pi K/(k_B T)]$, where a has dimensions of an inverse length, related to the surfactant size and k_B is the Boltzmann constant. This also allows comparing rigidity with thermal fluctuations. In turn, the ratio $k_B T/\xi_k^2$ marks a critical value for the surface tension, below which a single phase is expected with oil and water mixed down to the scale ξ_k and above which phase separation occurs. Even though no predictions were given as of what type of surfactant/cosurfactant mixture would give highly flexible interfaces, evaluating these parameters is important for obtaining disordered, rather than ordered, structures.

Taking inspiration from the work of De Gennes and Taupin, Ferroni and Baglioni developed the first microemulsion specifically formulated for the cleaning of artistic surfaces in 1986, during the restoration of frescoes in the Brancacci Chapel, in Santa Maria del Carmine Church (Florence) [6,43•,44]. The o/w microemulsion, where dodecane (ca. 10% w/w) was dispersed in a continuous aqueous phase (water content ca. 87% w/w) using dodecyl ammonium sulfate as surfactant and 1-pentanol (1-PeOH) as co-surfactant, was applied to remove wax spots from the wall paintings (see Figure 2). In this case, the removal of wax occurred via classic detergency, with the solubilization of wax within the swollen micelles of the microemulsions [6,29]. Besides the enhanced removal effectiveness, another important aspect is that the confinement of hydrophobic material inside the oil droplets hinders the re-deposition of the removed wax onto the painting substrate, as the continuous aqueous medium of the o/w microemulsion acts as a "hydrophilic barrier" [44]. Re-deposition of the removed grime/soil is also avoided by applying the o/w microemulsion loaded into highly sorbent materials, such as cellulose pulp poultices [15]; the sorbent extracts the dissolved and detached matter through capillarity, effectively removing it from the mural's matrix. Typical solvents used in the restoration practice have high evaporation rates (preventing their use in such poultices); therefore, solubilized matter is quickly re-deposited deeper within the pores of the murals as schematized in Figure 2. Finally, a significant advantage of o/w microemulsions as opposed to solvent blends is that high cleaning power is obtained with aqueous systems, where the solvent content is drastically reduced (typically 10–15%, but can be as low as 1% [43•]), and the impact on the operators and the environment is thus considerably decreased.

Starting from the Brancacci Chapel application, several microemulsions have been formulated through the last decades for the cleaning of artifacts, adapting to the removal of different types of unwanted layers [43•]. The formulation and application of these systems were supported by studies of their structure and on the mechanism through which they interact with different substrates, including soil, low molecular weight compounds (roughly in the molecular range 500–1000 Da, e.g. fatty acids, triglycerides, and terpenes found in natural varnishes [45]), and synthetic polymers, such as acrylate or vinyl acetate copolymers widely used in the restoration practice as adhesives and consolidants. In particular, the removal of aged polymeric consolidants has been extensively targeted, as polymer coatings are known to induce aesthetic alteration and degradation

Figure 2
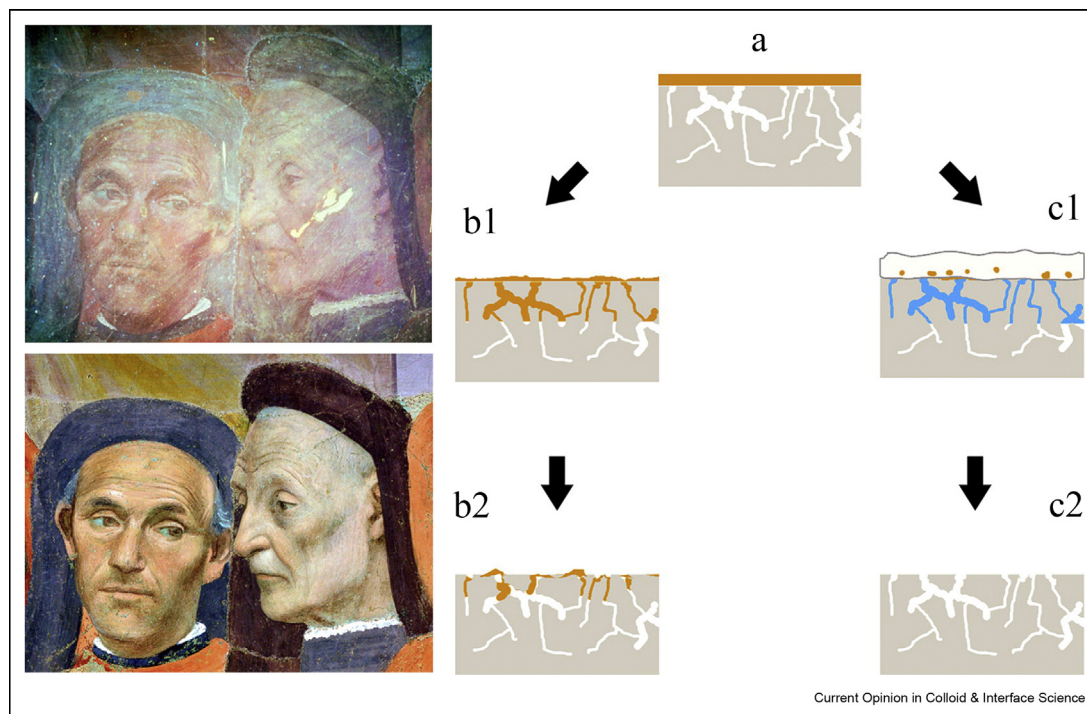
(Left) Details of wall paintings by Masaccio and Masolino in the Brancacci Chapel, Florence. The upper panel shows wax spots under UV light before cleaning. The lower panel shows the same area after cleaning with a microemulsion under visible light. (Right) Organic coatings on a porous substrate (a). On the left (b), the use of neat organic solvents causes the solubilization of the coating within the pores (b1 brown) and the redeposition of the dissolved coating within the substrate's pores upon solvent evaporation (b2). On the right (c), the continuous aqueous phase acts as a hydrophilic (c1 blue) barrier, preventing the penetration of the removed hydrophobic material within the porous substrate. The poultice acts as a sponge-like tool, further limiting the spreading of the removed polymer (c2). Adapted with permission from Ref. [43•]. Copyright 2013 American Chemical Society.

effects on wall paintings, in some cases even leading to the loss of the surface paint layers [6,15].

Regarding the structure of o/w formulations, small-angle neutron scattering (SANS) with contrast variation proved instrumental for elucidating how solvents and surfactants are placed in the dispersed and continuous phase of two different systems, featuring respectively a water-insoluble (xylene) and partially water-soluble solvents (ethyl acetate, EA, and propylene carbonate, PC), besides water, sodium dodecyl sulfate (SDS) and 1-PeOH [40••]. In both cases, micelles were initially modeled as monodisperse prolate ellipsoidal supramolecular aggregates with an effective charge and interacting through a screened Coulomb potential; the assumption is consistent with other studies on SDS/PeOH aggregates at similar concentrations, which exhibit preferential growth along one axis [46,47]. For the xylene containing system (p-xylene < 3% w/w, SDS ca. 4% w/w, and 1-PeOH < 8% w/w), fitting of the SANS data confirmed that the solvent, being immiscible with water, is confined in the micelles, and the ellipsoid aggregates in the water-SDS-1-PeOH system change to core–shell spheres after the addition of xylene [40••]; the system can thus be defined as a classical o/w microemulsion. Instead, in the system

featuring EA and PC (8% w/w each; SDS ca. 4% w/w, and 1-PeOH 7% w/w), the solvents are partitioned between the continuous phase and the dispersed micelles (partition coefficients of 0.7 for EA, and 0.3 for PC); therefore, the system was better defined as "swollen micelles". The presence of the solvents both in the continuous and the dispersed phase made the EAPC fluid particularly effective and versatile. Both formulations have been widely assessed in numerous case studies, as for instance the removal of aged and detrimental synthetic polymer coatings from murals belonging to European or Mesoamerican settings (see Figure 3a and b). The first studies on the interaction with EAPC and synthetic polymers involved a set of analytical techniques, from thermal analysis to scattering and microscopy [24•,29•]], which overall allowed picturing a multistep mechanism where swollen micelles exchange solvents with the polymer film, which in turn extracts an optimal solvent composition and swells, detaching from the surface; the micelles decrease in size and undergo structural rearrangement, whereas 1-PeOH has a role both in building the micelles and in removing the polymer.

The natural evolution in cleaning formulations was represented by the use of non-ionic surfactants, as their

Figure 3
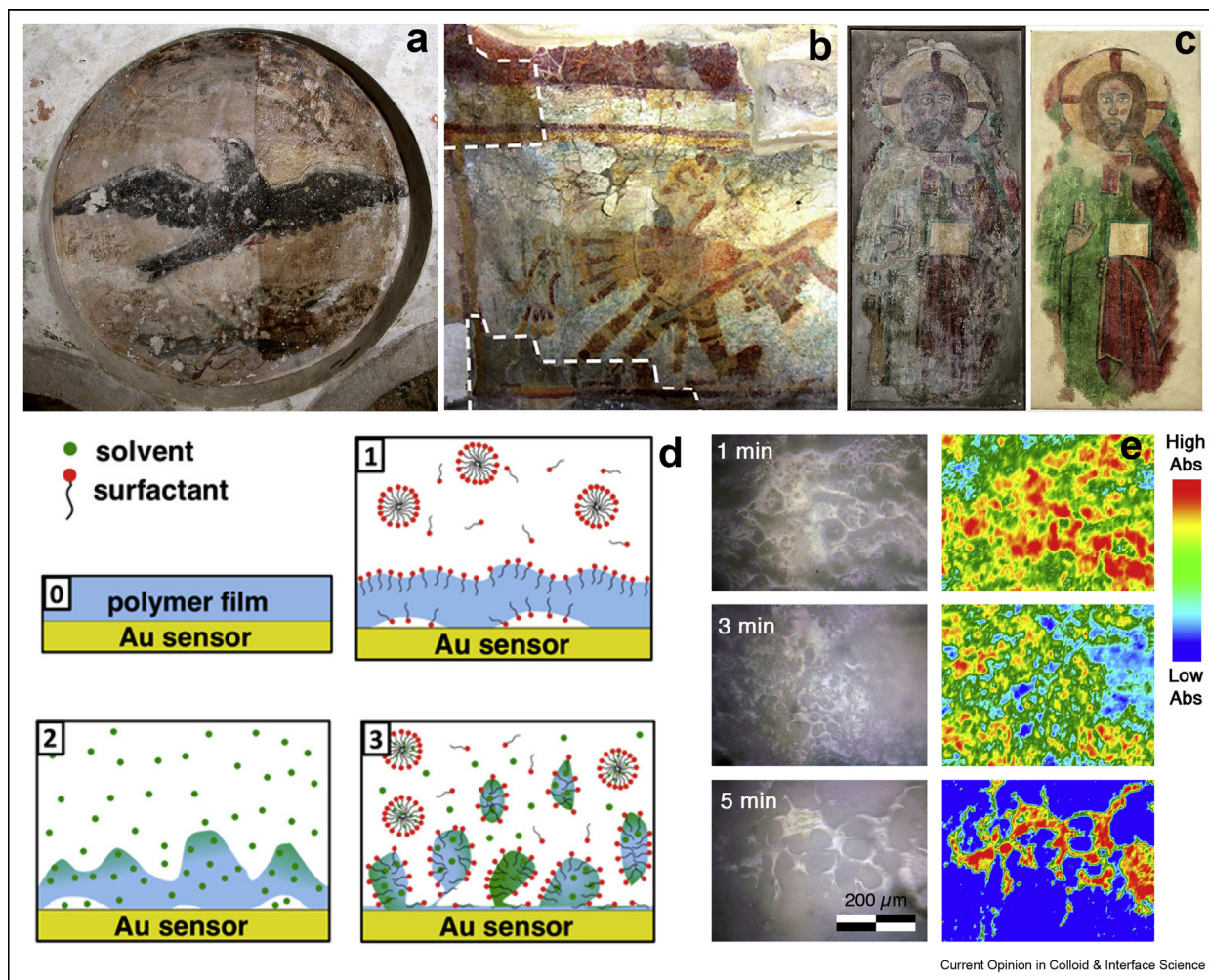
(a) Wall painting in the San Salvador church (Venice, Italy), before (right) and after (left) the removal of aged acrylate coatings. The use of an o/w microemulsion, containing xylene, SDS, and 1-PeOH besides water, allowed recovering the original painted surface that was jeopardized by the plastic-like appearance of the polymer coating. Reproduced with permission from Ref. [6]. Copyright 2013 The Royal Society of Chemistry. **(b)** Wall paintings in the Mayapan archeological site (Mexico). Detail of the removal of aged, detrimental polymer coatings using the "EAPC" o/w system (containing ethyl acetate and propylene carbonate). The dashed boxes highlight the small areas that were not cleaned and left untreated as a reference. Reproduced with permission from Ref. [24•]. Copyright 2013 American Chemical Society. **(c)** Detached fresco painting from the S. Cristoforo church in Milan (Italy), before (left) and after (right) cleaning and restoration. The cleaning was performed using an o/w system containing MEK and a narrow-range ethoxylated fatty alcohol surfactant, besides water. Reproduced with permission from Ref. [28••] Copyright 2014 The Royal Society of Chemistry. **(d)** Schematic representation of the proposed mechanism of polymer removal, in a quartz microbalance (with dissipation monitoring, QCM-D) experiment: (0) Polymer film on gold sensor before interaction with the liquid phase. (1) Morphological reorganization of the film induced by amphiphilic aggregates. (2) The good solvent penetrates within the film inducing a significant swelling of the coating. (3) The combined action of both surfactant and solvent promotes the detachment of the film from the surface. Reproduced with permission from Ref. 24•. Copyright 2017 American Chemical Society. **(e)** FTIR 2D imaging of mortar tiles coated with an acrylate copolymer (Paraloid B72®) and immersed in a water/$C_{9-11}E_6$/PC o/w system for 1 min, 3 min, and 5 min. Immersion for 5 min leads to partial or to complete dewetting of the copolymer from large portions of the surface (deep blue areas), leaving droplets and ripples of polymer. Each row shows the image of the surface under VIS light (left) and the FTIR map of the polymer peak at 1735 cm^{-1} (C=O stretching; right). Scale bar: 200 mm. The spatial resolution of the chemical maps is 5.5 μm. Reproduced with permission from Ref. [32••]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

phase diagram and solubility are less affected than that of ionic surfactants by the presence of salts (commonly found on the surface of murals). Besides, non-ionics self-assemble more readily both in solutions to form micelles, and at surfaces to form monolayers or bilayers, which makes them optimal for the removal of oily grime. Mixed ionic/non-ionic alkyl polyglycosides (APG) were used to formulate *p*-xylene-in-water microemulsions effective in the solubilization of naturally aged hydrophobic materials [48]. APG-containing microemulsions

with water content as high as >99% (w/w) were formulated and used to remove aged acrylic coatings from wall paintings. Amine oxide surfactants, widely used in detergents and cosmetics, were also considered as their aggregates have high dispersing power toward many water-insoluble organic substances and because of their degradability. In particular, a nanostructured fluid was formulated using water, diethyl carbonate (a green chemistry solvent, and a good solvent for medium—high polarity polymers), and N,N-Dimethyldodecan-1-amine oxide (DDAO) [49•]. Around neutrality, DDAO is only partly (ca. 20%) protonated and does not exhibit a cloud point, which can be advantageous for applications in environments with temperature higher than 20—25°C, where alcohol ethoxylates exhibit phase separation. In fact, the DDAO-containing system was used to efficiently remove aged coating of mixed synthetic polymers from wall paintings in the Maya archeological site of Tulum (Mexico).

More recently, broad-range (BR) and narrow-range (NR) fatty alcohol ethoxylates (C_iE_j) were used in o/w formulations with 2-butanone (also referred to as methyl ethyl ketone, MEK) [28••]. The NR and BR surfactants differed in homolog distribution, which was reflected in the different structures of their aggregates in the nanostructured fluids; at room temperature, the NR aggregates were elongated, whereas BR formed spherical and smaller micelles. However, these differences became almost negligible when the temperature distance of the systems from their cloud point was the same. SANS and nuclear magnetic resonance (NMR) analysis showed that MEK was dissolved in the aqueous continuous phase, rather than solubilized in the micelles; thus, it had a small effect on the size and shape of the micelles. However, changing the solvent concentration affected the cloud point of the formulations, e.g. from 20°C to 10°C when going from 8% to 20% MEK. Overall, the use of C_iE_j surfactants gave better cleaning results than formulations with SDS at the same MEK concentration. Besides, the NR C_iE_j was more effective than the BR, probably because the NR-MEK 20% system was closer to the cloud point, a condition that is known to enhance the cleaning performance. A formulation containing the NR surfactant was successfully used to remove aged polymer consolidants from a medieval fresco, as shown in Figure 3c. At that stage, it was already evident that other mechanisms than classical detergency were at play in the removal of polymer films by amphiphile-based nanostructured fluids. It was noted that the presence of the surfactant was essential for removal of synthetic polymers, an observation that led to further investigation of the interaction between these fluids and polymer films.

In particular, a series of recent studies focused on the mechanism of removal of Paraloid B72®, a 70:30 (w/w)

poly(ethyl methacrylate/methyl acrylate) (p(EMA/MA)) copolymer widely used in the restoration practice as an adhesive or coating, from a nonporous model substrate (glass). Three-components nanostructured o/w fluids (water/surfactant/solvent) were used, considering also the effect of each fluid's component and their combination on the removal process. Polymer films with controlled thickness were cast by spin coating, so as to have controlled and homogeneous thickness. These conditions were meant to study simpler frameworks than those met in real conservation cases, to clearly isolate relevant factors in the polymer removal process.

A combined quartz microbalance (with dissipation monitoring, QCM-D) and confocal laser scanning microscopy study investigated the specific role, in the removal of Paraloid B72®, of each component of a ternary formulation containing water, MEK, and either SDS or the BR C_iE_j [50•]. The two techniques provided complementary information, in that QCM-D was used to monitor the early stages of the fluid—polymer interaction, detecting adsorption/desorption of mass at the molecular level, whereas confocal microscopy revealed morphological changes in the polymer film at the microscale. The combined analysis evidenced that in the case of the BR-containing fluid, the surfactant has an active and specific role; it weakens intrachain and interchain polymer interactions, enhancing the mobility of chains and decreasing the interfacial energy at the swollen/bulk interfaces; the film is softened, and the penetration of water and MEK (a good solvent for the polymer) is promoted, overall producing the effective removal of the film (see Figure 3d). Interestingly, a completely different mechanism was highlighted for the SDS-containing fluid. In this case, the adsorption of SDS micelles on the surface of the polymer film hinders the access of MEK into the polymer layer; this was explained considering that SDS has less affinity for the hydrophobic polymer than BR. In fact, the anionic surfactant has a more pronounced hydrophilic character than BR, and electrostatic repulsion occurs between charged SDS micelles (or molecules) adsorbed on the polymer surface and those coming from the bulk solution.

Two following studies provided further insight, using confocal microscopy to look into the dewetting of the same acrylate copolymer from surfaces, induced by water/solvent mixtures in the presence or absence of amphiphiles [31••,32••]]. Polymer dewetting is desirable for cleaning applications as it leads to the disruption of unwanted polymer films and their detachment from the surface as swollen droplets. The process starts with the formation of interfacial regions between the polymer and the solvent (disfavored for nonsolvents) and between the substrate and the aqueous phase (favored for hydrophilic substrates); the detachment areas then evolve via nucleation and growth, coalescing until a

critical value is reached, after which complete dewetting takes place. While the dewetting of thin films (<100 nm) is known to occur in several conditions (e.g. thermal annealing, exposure to solvent vapors, immersion in poor solvents, water/solvent mixtures, or nonsolvents [51−53]), it was observed that the presence of surfactants in a water/good-solvent mixture can drive the dewetting of thick films (e.g. 5 μm), closer to those met in art conservation. The main focus was to clarify the role of surfactants in the thermodynamics and kinetics of the process. According to thermodynamics, depending on the polymer nature and on the type of polymer−substrate interactions, a polymer at temperatures higher than its glass transition (T_g) could dewet from a substrate simply using water or water/surfactant mixtures. Better solvents for the polymer give better swelling of the film, with higher mobility of the polymer chains, needed to achieve dewetting. It was clarified that the role of surfactant is central to kinetically drive the process; the surfactant lowers the interfacial energy between the involved phases, decreasing the activation energy barrier of the dewetting process, so that the barrier is overcome by thermal fluctuations of the polymer film stability [31••]. Thus, amphiphile-based formulations with very low surface tension can be particularly effective at dewetting polymer films, which can also explain why a $C_{9−11}E_6$ surfactant performed better than SDS [32••]. High concentration of surfactant seems to be not necessary, even if the process is faster at higher concentrations. Namely, for formulations with water-miscible organic solvents, it is possible to lower interfacial tensions working around the critical micellar concentration. Recently, a fluorescence correlation spectroscopy (FCS) study provided further detail on the dewetting process of the same acrylate copolymer when exposed to a nanostructured fluid containing water, propylene carbonate (a good solvent for the polymer), and $C_{9−11}E_6$ [54•]. It was found that the surfactant micelles are partially disrupted during the penetration of the fluid in the polymer film, and the consequent surfactant release swells the polymer chains, increasing their mobility. Besides, the non-ionic surfactant promoted the formation of interfacial defects with high interfacial area, both inside the film and at the film-substrate (glass) interface, promoting the dewetting of the film.

While the dewetting mechanism is being finely described, current studies are also targeting systems that are closer to real cleaning case studies than the models considered so far. For instance, dewetting patterns have been observed, using 2D FTIR imaging, even on mortar tiles coated with uneven and thick films of Paraloid B72® that were exposed to a water/$C_{9−11}E_6$/propylene carbonate system, mimicking the cleaning of wall paintings from aged coatings (see Figure 3e) [32••]. Other aspects recently investigated include the behavior of complex cleaning formulations (e.g. four or more components, including co-surfactants) in the removal of different types of polymers (acrylate and polyvinyl acetate copolymers) from substrates with different hydrophilicity/hydrophobicity (e.g. glass, marble, plastics) [55•]. It was shown that polymer films cast from solutions can be swollen by water/organic solvents mixtures or dewetted when a surfactant is added to the cleaning fluid. Films formed from polymer latexes are generally swollen even just by water but tend not to dewet, likely because the amphiphilic additives in the film formulations alter the energetic balance of the liquid/polymer/solid system, stabilizing the film. However, the swollen films are easily removed from the substrates, as the action of the fluids promotes loss of adhesion and detachment, similarly to what occurs in the first stages of dewetting.

Finally, water-in-oil (w/o) microemulsions have also been considered recently as cleaning systems, based on the rationale that these systems can be less risky on latex acrylic paints or modern oils, where contact with water can cause swelling or pigment pick-up [56,57•]. The confined aqueous phase in these systems can be added with chelating agents so as to increase its cleaning power, while the continuous apolar phase (e.g. hydrocarbons) has low swelling power and low solvency interaction on water-sensitive artistic layers. Formulations comprised water, the Shellsol® D38 solvent (mostly made of paraffins and naphtenes) as continuous water-immiscible phase, and different amphiphiles. Namely, either a linear alkylbenzene sulfonate surfactant (LAS, sodium dodecylbenzene sulfonate) or the ECOSURF®EH6 (Dow) non-ionic ethoxylated/propoxylated branched alcohol (2-ethyl hexanol) were used with two co-surfactants (1-butanol and 1-hexanol); sodium dioctyl sulfosuccinate was used without co-surfactants. It was concluded that the w/o formulations can limit to a degree the risks associated with aqueous cleaners, retaining the possibilities for exploiting the positive aspects of water-containing cleaning phases. While the practical evaluation of these systems will be the subject of future studies, one concern regards the high amount of surfactants needed to formulate the w/o microemulsions, i.e. ranging from 5 to 10% to more than 25% (w/w), and in some cases up to more than 50%, and the consequent rinsing steps needed to remove the residual surfactants from the surface after cleaning interventions.

The confinement of nanostructured fluids into retentive matrices

There are several cases where the use of cleaning fluids needs to be controlled in order to avoid damage to sensitive artistic substrates. Examples include paper artworks, watercolors, and some modern and contemporary latex or oil paintings, where original components such as inks, dyes, binders, or additives (including

Figure 4
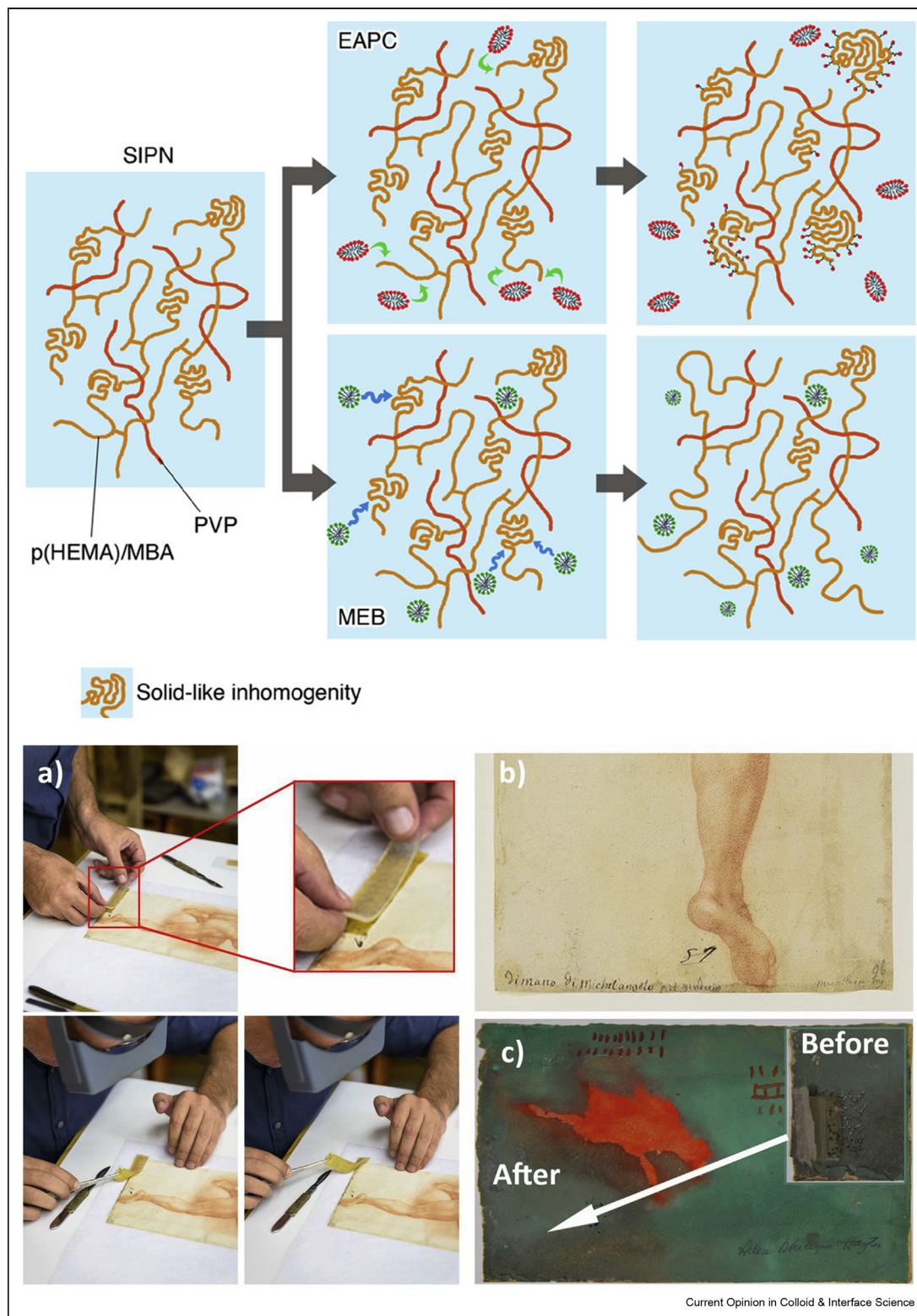
(Top) Cartoon illustrating the hypothesized interaction of two 5-components nanostructured fluids ("EAPC" and "MEB" systems, containing different solvents and surfactants) with a pHEMA/PVP semi-IPN hydrogel, according to SAXS data interpretation. In the case of EAPC, the average size of the inhomogeneities increases of about 10 nm after the loading of the fluid into the gel, because of a "micro-phase separation" of pHEMA, surfactant, and PVP, which generates a solid-like region. In the case of MEB, conversely, the solvents contained in the micelles promote the disentanglement of pHEMA inhomogeneities. Reproduced with permission from Ref. 71••, Copyright ® 2018 American Chemical Society. **(Bottom)** (a) Removal of a pressure

surfactants) can be swollen or leached by water and organic solvents. The traditional approach in the conservation practice consists in thickening solvents or aqueous solutions with polymers, so as to increase their viscosity and better control their cleaning action. Cellulose ethers have been recommended to thicken solutions of various types of surfactants; carboxymethyl celluloses with different grades and viscosities are used to impart thixotropic properties to aqueous solutions [18●]. Besides, a study reported on the inclusion of a xylene-in-water microemulsion in a viscous dispersion of hydrophobically modified hydroxyethylcellulose (hmHEC, 2% w/w) [58]. Only minor modifications in the nanostructure of the microemulsion were observed, i.e. a slight increase in polydispersity, size of the nanodroplets, and interdroplet spacing, which were ascribed to a partial inclusion of the hmHEC hydrophobic sidechains into the nanodroplets.

PAA is also used as a versatile thickening agent in the preparation of the aforementioned "solvent gels", along with cocoamine derivative surfactants [18●,36]. Both cellulose derivatives and PAA are typically used to prepare pasty "gel-like" viscous polymer dispersions that are applied and removed using swabs or spatulas. These systems are easy to prepare and have been widely used by restorers and conservators, but their application involves the need of rinsing steps with clearing solvents to remove polymer residues after the cleaning intervention, with possible alterations of the painted surface [15,59].

Lately, pickering silicone emulsifiers based on cyclopentasiloxane and dimethicone cross-polymers, such as Velvesil® and Shin-Etsu KSG®, have been used by conservators as they are less risky on water-sensitive surfaces [60]; however, cyclosiloxane solvents (e.g. D4 and D5, used also in rinsing steps) were recently restricted owing to their toxicity potential and environmental impact [61].

Polysaccharide-based networks such as agar and gellan are widely used to prepare physical gels (i.e. held by secondary bonds) that can be uploaded with aqueous solutions of chelating agents, enzymes or surfactants, and can be shaped as rigid gel sheets that are easily handled and removed from surfaces. However, these formulations proved to be either not enough retentive on highly water-sensitive and solvent-sensitive dyes [62] or too rigid to adapt to the rough, clotted surfaces frequently met in modern/contemporary paintings [63●].

Alternatively, gels with ideal mechanical behavior and retentiveness for the cleaning of works of art have been developed in the last decades in the framework of colloid science [14●●,27●,64●−66]. Polymer classes and synthetic routes were selected to have gels with tunable properties in terms of porosity, solvent uptake, and rheological behavior. Ideal formulations must be easily handled, used, and removed in one piece from the treated surface and must release gradually the uploaded fluids at the gel−artifact interface. The most effective gels, which were formulated based on these requirements, include physical and chemical (i.e. held by covalent cross-links) hydrogels, semi-interpenetrated networks (semi-IPNs) of physically or chemically cross-linked and linear polymers, and organogels (i.e. including organic solvents rather than aqueous fluids) [61,63●,67,68]. For instance, semi-IPNs made up of poly(vinyl pyrrolidone) (PVP) chains embedded in a poly(2-hydroxyethyl methacrylate) (pHEMA) chemical network were formulated as gel sheets that can be uploaded with water, water/alcohol blends, enzymes, and o/w nanostructured fluids [26●●,62,66,68−71●●]. In the latter case, rheological and SAXS measurements were carried out to study possible changes in the structure of the pHEMA/PVP semi-IPNs and two 5-component o/w fluids, i.e. the aforementioned EAPC and a fluid named "MEB" that includes DDAO as the surfactant, water, and a 1:1:1 mixture of MEK, EA, and butyl acetate [71●●]. Uploading the fluids did not alter the rheological properties of the semi-IPNs, and the tridimensional structure of the gels was preserved. Minor modifications of the gel network were hypothesized at the nanoscale, based on the SAXS analysis; uploading EAPC increased the average size of structural inhomogeneities in the semi-IPN of about 10 nm, possibly because of a "micro-phase separation" of pHEMA and surfactant, generating bigger solid-like domains; instead, loading with MEB caused the disentanglement of pHEMA inhomogeneities (see Figure 4, top). The presence in the two formulations of different surfactants and of solvents with different affinity to pHEMA and PVP probably determines different fluid−gel interaction mechanisms. Overall, because the micellar structure of the fluids was preserved, it was concluded that these semi-IPNs are able to behave as "sponges" that load the fluids and release them at controlled rate without dramatic alterations of their structure. The combination of the highly retentive semi-IPNs with the cleaning power of the nanostructured fluids makes these systems one the most sophisticated tools currently available for cleaning works of art. Recent applications include the removal of

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sensitive tape (PST) from the bottom of the 16th-century drawing. The detail shown in the red square highlights the EAPC-loaded hydrogel (pHEMA/PVP semi-IPN) shaped to precisely match the PST to be removed to avoid contact between the cleaning system and the artwork. (*b*) Detail of the drawing after removal of the PST, where the inscription "*di mano di Michelangelo*" appears, probably a false attribution that was concealed by the collector. (*c*) Contemporary drawing by Helen Phillips Hayter after removal of the PST. *Inset* shows the detail of PST before removal. Reproduced with permission from Ref. [26●●]. pHEMA, poly(2-hydroxyethyl methacrylate); PVP, poly(vinyl pyrrolidone).

Figure 5
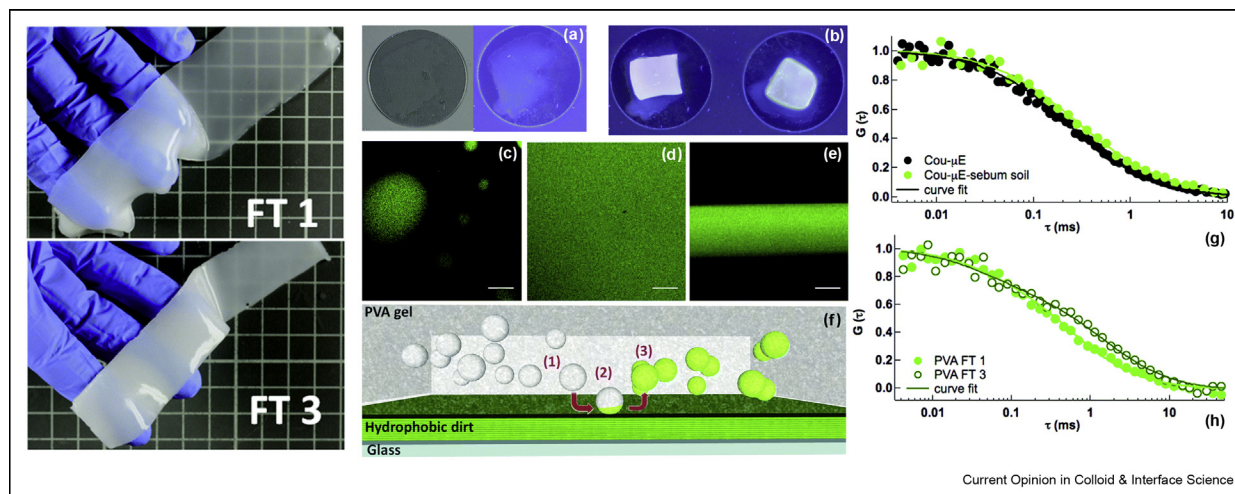
(Left) PVA-based gels, obtained with one (FT 1) or three (FT 3) freeze−thaw cycles. **(Center and right)** Interaction of microemulsion-loaded PVA gels with model dirty surfaces. (a and b) Representative pictures of (a) coverglass covered with a coumarin-labeled sebum soil layer under white (left) and UV (right) light, (b) the same coverglass with PVA FT1 (left) and PVA FT3 (right) gels layered on top; (c−e) representative confocal laser scanning microscopy images of the coumarin-labeled sebum soil layer ($\lambda_{excitation}$ 488 nm, $\lambda_{emission}$ 498−530 nm), as horizontal (c and d) and vertical (e) sections; (f) scheme representing the interaction of the microemulsion-loaded PVA gels with the labeled hydrophobic dirt: the unlabeled droplets (1) interact with the labeled dirt (2) and encapsulate the low-molecular weight labeled dirt (3); (g) representative fluorescence correlation spectroscopy (FCS) curves acquired for the free coumarin-labeled microemulsion before (black circles) and after (green circles) interaction with sebum soil-covered coverglass; curve fitting according to a one-component, before interaction with sebum soil, and two-component diffusion model, after incubation with sebum soil (continuous lines); (h) representative FCS curves acquired inside PVA FT1 (filled circles) and PVA FT3 (empty circles) gels loaded with unlabeled microemulsion after 10 min interaction with a coumarin-labeled sebum soil-covered coverglass; curve fitting according to a two-component diffusion model (continuous lines). Reproduced from Ref. [72•] with permission from the PCCP Owner Societies.

varnishes or pressure sensitive tapes from watercolors and paper artworks [26••,71••]; this type of intervention is problematic in the traditional restoration practice, but the use of retentive gels combined with o/w nanostructured fluids allowed for effective cleaning in a feasible way (see Figure 4, bottom).

Poly(vinyl alcohol) (PVA)-based gels are another class of materials that lately gained attention in art cleaning applications [62•,72•]. Gels with high viscoelasticity and flexibility can be prepared via freeze-thaw (FT) gelation of PVA solutions; remarkably, these cross-linked networks are held by secondary bonds (e.g. H-bonds), but exhibit a rheological behavior typical of solid-like chemical networks. Through the FT process, it is possible to obtain sheets (see Figure 5) that can easily adapt to the 3D textured and clotted painted surfaces frequently found in modern/contemporary art and are easily removed from the treated surface without leaving detectable residues (as checked with infrared imaging), overcoming the limitations of traditional pasty polymer dispersions and "rigid" gel sheets (e.g. gellan) used in the restoration practice [62•]. Similarly to pHEMA/PVP semi-IPNs, it is possible to upload the PVA FT gels with o/w microemulsions, so as to target the removal of hydrophobic substances. The dynamics of a toluene-in-water microemulsion loaded in the gels were recently

studied using confocal laser scanning microscopy and FCS [72•]. FCS curves were acquired for the labeled microemulsion before and after interaction with a sebum soil film (Figure 5). The droplets embedded in the polymeric matrix are freely diffusing and available for interaction with soil, after which a slight increase in the decay time of the curves occurred. After interaction, a two-component diffusion model was used to describe the dynamics of the microemulsion, with a first component because of the unmodified system, and a slower component because of a an increase of the droplets' size as they include the solubilized soil. PVA FT gels were recently used, either loaded with aqueous solutions or o/w microemulsions, to effectively and safely remove surface soil or aged coatings from the surface of masterpieces by Jackson Pollock and Pablo Picasso [73].

Perspectives: biodegradable and self-cleavable surfactants

Improved biodegradability has been behind most of the industrial efforts to introduce into the surfactant structure an ability to undergo spontaneous degradation. Surfactants that degrade spontaneously are sometimes referred to as "cleavable surfactants" or "labile surfactants", and the degradation is usually caused by acid-catalyzed or base-catalyzed hydrolysis of the bond that

connects the polar headgroup with the hydrophobic tail. The aim has primarily been to promote the surfactant degradation in sewage plants, so that it will not accumulate and will be easily digested by the microorganisms. A well-known example is the diesterquats, in which ester bonds link the hydrophobic tails to the polar headgroup [74]. However, the biodegradability issue is only of minor importance when it comes to development of cleaning formulations for art conservation, as the volumes released into the effluent will be negligible compared with the use of surfactants in detergency and other large volume applications. These efforts have, however, resulted in a toolbox of commercially available surfactants that are safer not only for the environment but also for the users, as these two aspects are often interrelated.

From the conservators' perspective, the concept of labile surfactant has more important implications when it comes to the question of the presence of residues on the surface, e.g. remains of surfactants, which, contrary to the solvent in the cleaning formulation, are not volatile. In that scenario, cleavable surfactants, and in particular self-cleavable surfactants, i.e. surfactants programmed to degrade with time, are of great interest. Ideally, the surfactant will decompose into volatile products, but even if that is not the case, the remains on the surface of the work of art will not be surface active and will be chemically inert. A subsequent rinsing step will then probably not be needed. Decomposition by hydrolysis will require water, either as traces left on the surface or provided by the ambient humidity.

When designing cleavable surfactants, there is a wide range of chemical bonds to choose from and the choice will be governed by the conditions of use, such as temperature and pH. Bonds susceptible to either high or low pH are commonly used as weak linkage. In the case of cleaning formulations applied to works of art, there are severe limitations with respect to both pH and temperature because the object to be cleaned usually cannot stand extreme conditions and also the conservators cannot work in an unhealthy environment. The pH should be in the range 4–9, and the temperature should not exceed 35°C, which limits the type of cleavable bond to choose from. Among the different types of labile bonds, the most susceptible to hydrolysis is the orthoester and the carbonate bonds, which undergo hydrolysis on the acidic and alkaline side, respectively. Typical structures of such surfactants are displayed in Figure 6a and b. In the case of the carbonate surfactant shown in Figure 6b, the degradation products are carbon dioxide and octanol, which are volatile and tetra(ethylene glycol). Tetra(ethylene glycol) is not volatile but is non-toxic, readily biodegradable, and completely inert. Interestingly, the carbonate bond has been found to give the same contribution to hydrophobicity as a methylene groups [75●].

Another appealing approach is to take advantage of the surfactant cleavability to control the surface activity and by that, the cleaning efficiency of nanofluids. Gemini surfactants, sometimes referred to as dimeric surfactants, are amphiphiles that consist of two regular surfactants connected at the headgroups by a short spacer unit [76]. A gemini surfactant is considerably more efficient than the monomeric counterpart, i.e. the surface tension of a gemini surfactant at low concentration is much lower than that of the monomer at the same concentration [74]. If the spacer unit contains a cleavable bond, the degradation of the gemini surfactant will generate another surfactant that is less efficient, i.e. gives a higher surface tension at low concentration.

This approach was used for the design of a cleavable surfactant with the weak linkage, a carbonate bond, in the spacer unit. As mentioned above, a carbonate bond is very susceptible to alkaline hydrolysis, and unlike ester-

Figure 6
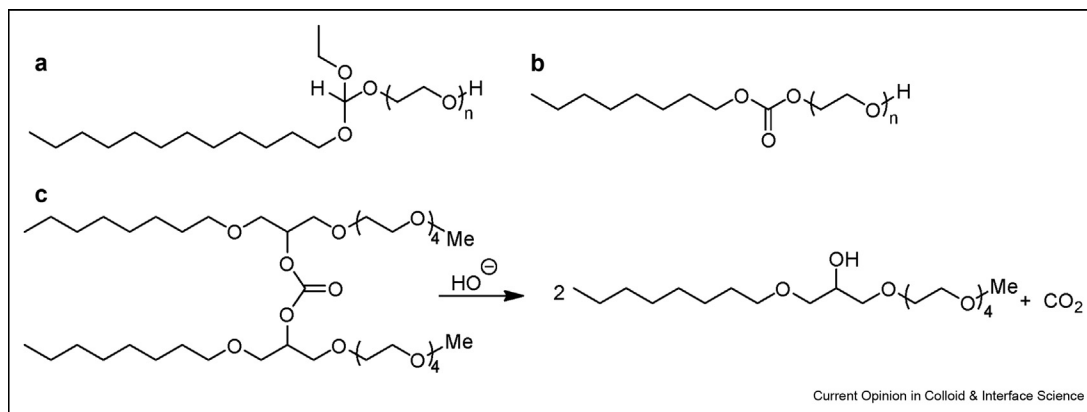
(a) An orthoester susceptible to acidic hydrolysis. **(b)** A carbonate surfactant susceptible to alkaline hydrolysis. **(c)** A gemini surfactant where the two monomeric units are linked by a carbonate bond and its degradation through alkaline hydrolysis.

based surfactants, the degradation products are nonacidic, which is an advantage for cleaning of sensitive surfaces. Already moderately alkaline conditions, such as those of a cleaning formulation, will induce hydrolysis of the carbonate bond, generating the monomeric surfactant, which at low concentration is much less surface active than the starting gemini surfactant. The concept is illustrated in Figure 6c.

The gemini surfactant was prepared in a two-step approach; first, a single tail surfactant having glycerol as a linker between the polar headgroup and the hydrophobic tail was prepared. In a second step, the gemini surfactant was formed by reaction with phosgene, which connected the two secondary hydroxyl groups by a carbonate bridge. With 4 oxyethylene units and an octyl tail on each monomer, the gemini surfactant had a cloud point close to room temperature, which is suitable for cleaning purposes. The degradation was rapid under slightly alkaline conditions, as monitored by NMR and by the increase in surface tension, and contrary to expectation, the rate of degradation was much faster at 15°C than at 30°C. This was explained as an effect of decreased solubility of the non-ionic amphiphile with increasing temperature, which, in turn, is because of reduced hydration of the oligo(ethylene glycol) chain at higher temperature [77•]. Carbonate-based gemini surfactants have not yet been tested in cleaning formulations for works of art, however.

Conclusions

The contribution of soft matter and colloid science to the conservation of cultural heritage has been of paramount importance in the last decades. In particular, advanced systems have been formulated for the cleaning of works of art, where the selective and noninvasive removal of unwanted layers from the surface of the works are fundamental requirements. Surfactants play a key role in the formulation of oil-in-water (o/w) aqueous cleaning fluids and in their interaction with soil, hydrophobic grime, and aged/detrimental natural or synthetic products present on the artifacts from past restoration interventions. In particular, nanostructured o/w cleaning fluids have been formulated using different types of ionic and non-ionic surfactants and co-surfactants. In these systems, organic solvents are either confined in nanosized droplets (if water-insoluble) or partitioned between the dispersed phase and the continuous aqueous phase (if partly water-soluble). The cleaning power, safety, and environmental friendliness of o/w microemulsions and swollen micelles are enhanced as compared with the traditional solvent blends used in the daily restoration practice. The removal of unwanted layers takes place through mechanisms that range from the solubilization of grime and low-molecular weight compounds in the micelles to the swelling or dewetting and detachment of aged

polymer layers from artistic surfaces. In polymers dewetting, surfactants in o/w fluids have been shown to favor the kinetics of the process, lowering the interfacial energy of the involved phases. Water-in-oil fluids have also been considered for applications on water-sensitive painted layers, the rationale being the confinement of water in droplets dispersed in continuous apolar (hydrocarbon) phases.

The effectiveness of these advanced cleaning tools has been assessed in numerous case studies, concerning classic and modern/contemporary art, and some protocols on the use of microemulsions and gels have been provided to the conservation community. The latest improvements involve the confinement of nanostructured fluids in retentive gel matrices and the development of biodegradable and self-cleavable surfactants. Retentive gels are able to behave as sponges, uploading the cleaning fluids and releasing them at controlled rate onto water-sensitive and solvent-sensitive surfaces, such as watercolors, inked paper, or some latex paints. Biodegradable and self-cleavable amphiphiles, such as gemini and carbonate surfactants, contribute to further reduce the ecotoxicological impact of the fluids and might eliminate the need of rinsing steps in cleaning interventions.

Overall, the possibilities offered by colloid science allowed overcoming the limitations of traditional cleaning methodologies based on classic solution and polymer chemistry, but the proposed solutions are also of interest in numerous fields beyond cultural heritage conservation, ranging from detergency to cosmetics and drug-delivery.

Conflict of interest statement

Nothing declared.

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This work deepened the role of surfactants in the dewetting of polymer coatings by nanostructured cleaning fluids. In particular, two different surfactants (ionic and non-ionic) and two different solvents were combined to investigate the role of solvents and surfactants in the process from a thermodynamic and kinetic standpoint. Besides, the first systematic observation of polymer dewetting for thick films on representative substrates (mortars) was provided by means of infrared 2D imaging.

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This contribution collects the work done since the 1980s by the author, including some of the first aqueous systems containing surfactants that were specifically formulated for the cleaning of art.

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●● **structured surfactant-based systems for the removal of polymers from wall paintings: a small-angle neutron scattering study**. *Langmuir* 2012, **28**:15193–15202.
This work clarified the structure of two oil-in-water cleaning fluids that have been largely used in cleaning case studies. In particular, it was shown that different structural features play a key role in defining the kinetics of interaction between the fluids and polymeric coatings, which is of paramount importance for the application in the field.

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This work was inspirational to the formulation of oil-in-water fluids for the cleaning of works of art. The authors proposed two main principles that must be satisfied for the formation of a microemulsion from a water + oil + surfactant system.

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43. Baglioni P, Chelazzi D, Giorgi R, Poggi G: **Colloid and materials**
● **science for the conservation of cultural heritage: cleaning, consolidation, and deacidification**. *Langmuir* 2013, **29**:5110–5122.
The article reviews the first application of an oil-in-water microemulsion formulated for the cleaning of wall paintings, and reports on several case studies that illustrate the effectiveness of these systems either non-confined or confined in retentive gel matrices.

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The authors studied in detail the degradability of a new gemini surfactant with a carbonate linkage, which is appealing for art cleaning purposes. An unusual behavior was found, i.e. alkaline hydrolysis is rapid at 15 °C but very slow at 30 °C, with a reverse relationship between rate of hydrolysis and temperature.