Micellar solutions as environmentally-friendly agents for cleaning artworks

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ABSTRACT

The research presented in this communication is part of a major research project aimed at the application of nanoscience for the preservation and consolidation of the materials of cultural heritage objects, mainly the artifacts from limestone, sandstone, marl, etc. The project encompasses all the main fields important from the point of view of protection of cultural heritage, especially the cleaning the surface of historical materials, their consolidation and preventive protection. Our approach to the preparation of cleaning mixtures is based on the combination of two components, the “standard” micellar solution or microemulsion of nonionic surfactants with co-surfactants added, which is practically the same for various target substances and the specific solvents selected according to the respective substance to be removed. Based on this approach, a cleaning mixture was elaborated based on the joint action of micelles of non-ionic surfactants, 1-pentanol and acetates, which is able to effectively remove and solubilize layers of acrylates.

Keywords: Conservation of cultural heritage, cleaning, micellar solutions, nonionic surfactants, polyacrylate copolymer.

1 INTRODUCTION

Conservation science is one of the most complex topics in the materials science as it requires expertise ranging from the history of art and archaeology to the advanced analytical and physical chemistry. However, the recent development has shown that the complex tasks of the conservation of the cultural heritage can be solved very effectively and as friendly as possible towards the treated artifacts and the environment using novel nanomaterials and nanotechnology procedures. [1, 2]

In recent years the research effort has included the application of nanoscience in all the main fields important from the point of view of protection of cultural heritage, especially the cleaning the surface of historical materials, their consolidation and preventive protection (against the action of water, the deposition of dirt, biodegradation etc.)

The requirements which should be met are rather demanding. The cleaning procedures should remove cautiously but effectively the dirt, corrosion products and remnants of earlier, sometimes unsuitable or already weathered, conservation measures. The consolidation nanomaterials should be compatible with the treated artifact and ensure a highly stable conservation of the heritage materials degraded by the atmospheric action and biodegradation. The impregnation of the porous inorganic substrate with sols containing nanoparticles based on inorganic oxides and hydroxides has provided promising results. The nanostructured surface coatings minimize the retention of microflora and microfauna on the surfaces of both historic and modern monuments. Biocide agents based on metal nanostructures ensure a controlled release of the active component at an optimum concentration during a very long time.

The present communication is aimed at one of the most important aspects of the conservation of historic artifacts, namely at the micellar solutions suitable for the cleaning of the surfaces of historic materials. As the target substance to be removed, poly-ethyl-methacrylate/poly-methyl acrylate copolymer with average molecular weight of 80 000 (Paraloid B-72) was chosen. The use of this type of polymer has been very popular among restores, despite their adverse effects due to their poor physicochemical stability. [3] The removal of aged polymers, which is mandatory for the restoration treatments, is usually very difficult. The cleaning mixtures developed for the removal of this polymer should be simpler than those published and based on cheap and environmentally friendly reactants.

2 STATE OF THE ART

Since early 2000s the group of Baglioni and Dei has pioneered the use of micellar solutions and microemulsions for cleaning artworks, especially for the selective removal of aged polymeric coatings from the surface of wall paintings [1-11]. Micelles and microemulsions have been shown able to solubilize polymers and to achieve their complete removal from the surface and the porous structure of the artifact. Owing to their large surface area, the micelles have a great detergence capacity, which is usable for the interaction with the polymeric coatings. As the micelles are dispersed in an aqueous system, the penetration of polymeric materials to be removed into the porous structure of cleaned artifact is maximally reduced. The amount of the organic solvents used is decreased by 80-95%, which consequently drastically reduces the environmental impact.

One of the most successful cleaning systems developed by Italian scientists called EAPC consisted of sodium dodecylsulfate, 1-pentanol, ethyl acetate, propylene carbonate and water [11]. It was successfully used in the removal of vinyl acetate/n-butyl acetate copolymer Mowilith DM5 from the Maya mural paintings discovered in Mexico. This copolymer should serve as a protective and consolidating agent and was coated on the paintings at the end of the 1990s. However, within less than ten years it was necessary to remove it not to endanger the integrity of the paintings.

Baglioni and co-workers schematized the interaction mechanism [11]. Solvents dissolved in the continuous aqueous phase in equilibrium with dispersed nanodroplets interact with the polymer coating. In the mechanism suggested the authors include a series of exchanges with solvents migrating from the aqueous phase to the polymer to be removed, from the nanodroplets serving as solvent nanocontainers to the aqueous phase and from the nanodroplets to the polymer. The polymer coating "selects" an optimal composition and amount of solvents which leads to swelling and peeling off from the substrate. Due to the flow of the solvents from the nanodroplets have to reorganize their structure, which leads to a decrease in their size. In the mechanism suggested the role of nanodroplets is crucial as they enable that the right amount of organic solvents is dispersed in water and available for the interaction with the polymer. The mixture of solvents which is absorbed by the polymer is expected to be chosen by the physical-chemical characteristics of the polymer itself. [11]

For a controlled release of microemulsions and micellar solutions, which is required especially for the cleaning of paintings on canvas or wood, Baglioni et al have suggested their confinement into the network of chemical gels. Such gels are based e.g. on the poly(vinyl alcohol)-borate systems. [6]

3 RESULTS AND DISCUSSION

Our approach to the preparation of cleaning mixtures is based on the combination of two functions which are realized by two components

- the "standard" micellar solution or microemulsion of nonionic surfactants with co-surfactants added, which is practically the same for various target substances (such as the polymers to be removed from the surface),
- the specific solvents selected according to the respective substance to be removed.

There are several advantages of this approach, namely the substantially facilitated formulation of the cleaning mixtures, easier preparation and better understanding of the mechanism of their action. Prospective production in larger amounts would be easier and economically more favorable.

Owing to their outstanding features, nonionic surfactants are often more convenient than the ionic ones. Their main advantages are the very low critical micelle

In Table 1 there is an overview of nonionic surfactants presented, which were used for the preparation of micellar solutions. Their critical micelle concentrations were determined from the dependence of the surface tension of their aqueous solutions on their concentration.

The "standard" micellar solution was prepared by dissolving the selected nonionic surfactant in water at concentration several times exceeding the critical micelle concentration with suitable co-surfactant added, such as 1-pentanol.

For the most common anionic surfactant sodium dodecylsulphate, whose micelles have slightly non-spherical shape (theoretical diameter of micelles equals 3.7 nm, the experimental aggregation number being 74), some change in the shape and an increase in the size up to 10 nm were found to occur due to the addition of co-surfactants. However, no more complicated amphiphilic structures were formed, which seems due to the repulsive electrostatic forces and a too low concentration of the surfactant.

For non-ionic surfactants such as block-copolymers (Table 1) the addition of co-surfactant such as 1-pentanol leads to its solubilization in the core of the micelles and consequently to a substantial change in the size and probably also tin shape of micelles. The increase in the size of micelles of non-ionic surfactants seems to enhance the attractive forces arising between uncharged amphiphilic surfaces. Due to these forces larger structures are formed, such as liposomes and superaggregates, and coexist with the smaller aggregates or monomers in the solution. [12] While the smaller micelles are clearly favored entropically, the superstructures can be thermodynamically more favorable.

If M and **M** are the micelle and liposome aggregation numbers, than equating the chemical potentials of molecules in monomers, micelles and liposomes, respectively, gives in the equilibrium [12]

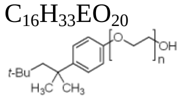
$$\mu_1^o + kT \log X_1 = \mu_M^o + (kT/M) \log (X_M/M) =$$

$$= \mu_{\mathbf{M}}^o + (kT/\mathbf{M}) \log (X_{\mathbf{M}}/\mathbf{M}) \quad (1)$$

The concentration at which $X_M = X_{\mathbf{M}}$ is

$$(X_M)_{crit} \approx M \exp[-M(\mu_M^o - \mu_{\mathbf{M}}^o)/kT] \quad (2)$$

Table 1. An overview of nonionic surfactants used for the formulation of cleaning mixtures

Surfactant	Chemical formula	M / g/mol	cmc / g/L
Pluronic P123	$EO_{20}PO_{70}EO_{20}$	5750	0.3
Pluronic F108	$EO_{133}PO_{50}EO_{133}$	14800	45.0
Pluronic F127	$EO_{106}PO_{70}EO_{106}$	12600	7.0
Brij 58P	$C_{16}H_{33}EO_{20}$	1124	0.086
Triton X-114		537	0.09

EO = ethylene oxide, PO = propylene oxide, M = relative molecular mass, cmc = critical micelle concentration.

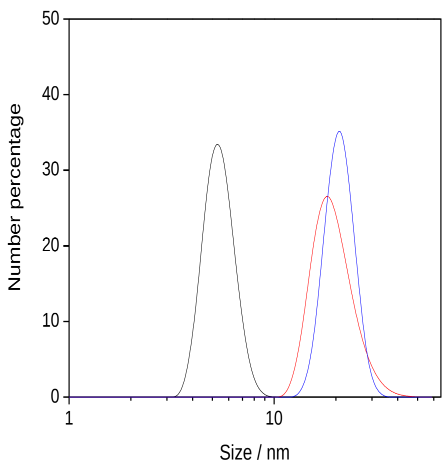


Fig. 1 Size distribution of micelles of Pluronic copolymer. (black) Pristine copolymer, (red) copolymer + 1-pentanol, (blue) copolymer + 1-pentanol + ethylacetate.

Thus depending on the aggregation number of micelles M and the difference in the standard parts of the chemical potential in the micelles and liposomes (μ_M^o - $\mu_{\mathbf{M}}^o$), the latter may form spontaneously at $(X_M)_{crit}$, corresponding to the second critical micelle concentration, while the concentration of monomers or small micelles remains unchanged. [12]

The formation of large liposomes several micrometers in size besides the smaller micelles was observed for, e.g., Pluronic P123 and Brij 58P, after the addition 1-pentanol serving as a co-surfactant.

According to the substance to be removed the specific solvents were selected which are able to dissolve it effectively and are compatible with other components of the cleaning mixture. For polyacrylate copolymer Paraloid B72 such solvent is ethylacetate. Ethylacetate seems only partially solubilized within micelles or larger aggregates, as its has only slight effect on the size of aggregates.

Fig. 1 shows the size distribution of micelles of Pluronic copolymer and the effect of added co-surfactant 1-pentanol and the specific solvent ethylacetate. The effect of the 1-pentanol added is pronouced, while that of ethylacetate practically negligible. In the figure the much larger superstructures, whose size achieves the micrometer range, have been omitted.

To test the ability of the cleaning mixtures to swell and disintegrate the polymeric layer, to detach it from the support surface and finally to solubilize it in an organic layer, several techniques were combined. A 5 or 10 %-solution of the polymer in a suitable solvent (toluen) was either introduced into a glass vial or deposited on several types of stones corresponding to building materials typical for historical buildings and sculptures (sandstones, limestones, marble). After the depositing the samples were dried at 65 ^oC for several days to quantitatively evaporate the solvent. The polymer amount deposited was 35 mg per cm^2 or a multiple of this amount.

After the evaporation of the solvent the cleaning mixture was added in different ratios to the amount of deposited polymer. Within several hours an organic phase separated. The efficiency of the cleaning was followed visually and the substance to be removed solubilized in the organic layer was identified by ATR-FTIR spectroscopy. To obtain quantitative data the amount of polymer removed fro the surface of stones was determined gravimetrically.

Based on an extensive optimization study, several efficient cleaning mixtures were developed. For the removal and solubilization of Paraloid B72 the mixture consists of the micellar solution (containing poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer Pluronic P123 (Table 1) and co-surfactant 1-

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pentanol solubilized inside the micellar core and ethylacetate, which is the specific solvent able to degrade the Paraloid B72 deposits. A comparative testing has shown that this mixture is more efficient than the EAPC one developed for the cleaning of wall paintings in Mexico (vide supra).

It was found that the presence of both 1-pentanol and ethylacetate is essentially important. Ethylacetate alone dissolved in a water solution of non-ionic surfactants only swells the acrylate copolymer, however the solubilization, which is viable for an effective removal of the polymer from the surface, does not occur. Therefore the presence of 1-pentanol is very important. Based on the understanding of the role of individual components, a cleaning mixture with the optimum performance can be formulated.

From following the dependence of the degree of the removal of the polymer from the surface on the amount of the cleaning mixture used and the length of its action it followed that for a complete cleaning of the surface an amount of 7 mL of the cleaning mixture per 1 mg of the polymer acting for two hours is sufficient.

4 CONCLUSIONS

To sum up, it follows both from the published data and our own research, that the cleaning mixtures based on micellar solutions of nonionic surfactants with a suitable co-surfactant and specific solvents added are able to remove very efficiently coatings of several selected substances important from the point of view of the conservation praxis. The systems based on nonionic surfactants are in laboratory tests more efficient in the removal of Paraloid B72 than published formulation based on ionic surfactants.

Our approach to the formulation of cleaning mixtures based on the combination of the “standard” micellar solution or microemulsion of nonionic surfactants with co-surfactants added and the specific solvents selected according to the respective substance to be removed is rather general.

Step by step the range of substances to be removed is widened. According to the needs of the conservation practice in the Czech Republic and abroad several other target substances were selected, namely terpenoid resins, linseed oil (triglyceride of unsaturated fatty acids), waxes as well as various polymers.

The first tests carried out on real heritage artifact have shown that the method presented has a promising potential for the application in the conservation practice.

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