Assessment of agar gel loaded with micro-emulsion for the cleaning of porous surfaces

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Introduction

1 During my training at the Wereldmuseum of Rotterdam, I had the opportunity to experiment with some mixtures made with agar and micro-emulsion. These experiments are reported in this paper.

2 For the cleaning purposes, the nature of porous surfaces forced the conservators to look at solubility, capillary action and evaporation rate of their materials and tools. The use of pure organic solvents can have the undesirable effect, typical of the surface considered, of redistributing the dissolved material further within the porous matrix.

3 This research focuses on the removal of hydrophobic materials on a porous and hydrophilic surface. We studied an agar gel loaded with a micro-emulsion. The agar gel was chosen for its common use in cleaning and its safety, and the micro-emulsion for the good results in the cleaning of porous paint layers. The purpose of the research was to improve the strength, the capability to retain the solvents and the efficacy of the agar gel loaded with micro-emulsion to remove wax, as well as to prevent the redistribution of this hydrophobic material into the porous layer.
Materials and methods

Micro-emulsion

Materials: Reverse Osmosis water, sodium dodecylsulphate (SDS, Fluka, purum ≥ 96 %), pentan-1-ol (Fluka, ≥ 99 %), Petroleum ether (Fishersci, 100/140 °).

Micro-emulsions are microheterogeneous liquid systems, which means structured systems of colloidal dimensions formed when amphipathic substances are dissolved in solvents, in appropriate concentrations. Among these microheterogeneous systems we may list the emulsions, the micro-emulsions and the micelles.

The first use of a micro-emulsion in the conservation field is mentioned by L. Borgioli for the cleaning of the Masaccio’s frescoes in the Brancacci Chapel. The cleaning of these paintings includes the removal of hydrophobic impurities (wax) using micro-emulsions. The Micro-emulsions were used later by E. Carretti for the removal of deteriorated organic materials, oil- and acrylic-based materials from mural paintings.

The most innovative aspects of the used of micro-emulsion are:

- A higher extracting efficiency of hydrophobic materials than emulsions.
- The redistribution of dissolved hydrophobic materials into the porous surface is avoided by the hydrophilic barrier of the continuous phase since dissolution takes place within the micelles aggregation.
- Micro-emulsion systems are thermodynamically stable throughout a wide range of environmental conditions.

Oil-in-water micro-emulsions contain a continuous phase (water) and a dispersed phase (aliphatic hydrocarbon) presents within the core of micelle aggregates of surfactant. The content of surfactant is much higher than the Critical Micelle Concentration. It causes the spontaneous aggregation of these molecules and reduces the interfacial tension between oil and water. A micro-emulsion can contain a co-surfactant in order to maximize the concentration of the dispersed phase in the system and lower the interfacial tension between water and oil droplets.
The dispersed phase forms micro-droplets in the continuous phase, coated by a mixed film of surfactant and co-surfactant. The size and shape of the micelles are a function of the concentration and structure (length and volume of the hydrophobic tail) of the surfactant; the droplets diameters are typically from 5 to 50 nm\(^5\). In the case of SDS as the surfactant, the micelles are spherical. The micelle size of SDS/Pentanol micro-emulsion, obtained from small-angle X-ray scattering, is about 4 nm\(^6\).

Addition of co-surfactant is not needed to form micro-emulsion, although it is used to simplify the work. The solvent Pentanol, a medium-chain length alcohol, changes the size of the micelles: smaller with a low concentration, bigger with a higher one\(^7\). The Pentanol molecules are located at the head at the surface of the micelle whereas the tail is penetrating the micelle core in the case of an oil-in-water micro-emulsion.

In the case of oil-in-water micro-emulsions, the dissolution sites may be identified in several regions:\(^8\): between the hydrophilic groups and the first carbon atoms of the alkyl chains of surfactants – in this region large aromatic molecules and long chain alcohol can be dissolved –, within the core of the droplets – dissolution of aliphatic hydrocarbons in the case of oil-in-water micro-emulsion –, and in the large hydrocarbon volume. The type of hydrophobic sites exhibited by micro-emulsion explains the high dissolving capacity of these systems. Moreover micro-emulsion systems are strongly dynamic which means that the components can show different kinds of exchange processes. The dynamic behavior of micro-emulsions controls the exchange of solubility between droplets, and it has a strong impact on the chemical reactivity of such systems\(^9\).
For conservation purposes, micro-emulsion with SDS (\(NaC_{12}H_{25}SO_4\)), as an anionic surfactant, and Pentanol (\(C_5H_{12}O\)), as the co-surfactant, were used. The micro-emulsion is prepared using the amount of materials indicated as in Table 1, the compositions are given in % of weight\(^{10}\). The micro-emulsion is stable and transparent.

Table 1 Composition of the oil-in-water micro-emulsion

<table>
<thead>
<tr>
<th>Continuous phase</th>
<th>Surfactant (SDS)</th>
<th>Co-surfactant (1-Pentanol)</th>
<th>Dispersed phase (Petroleum ether)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO water</td>
<td>85</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>(\mu E_1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Preparation of the gel**

The name “agar” refers to a complex mixture of polysaccharide components, which may be derived from certain genera of the Rhodophyceae group of red sea weeds\(^{11}\). The principal gelling component is Agarose based on a disaccharide repeat unit.

Fig. 2 Disaccharide repeat unit of Agarose

Credits: Clark, 1987

The thermoreversible gelation of Agarose occurs when hot Agarose solutions are cooled below about 40°C. The Agarose network structure involves a double-helix formation.
The agar gel is known to present large pore sizes which may allow the microemulsion to migrate to the surface of the gel that is in contact with the porous surface.

In this research, in order to test the faculty of agar gel to be loaded with micro-emulsion, five agar gels were be loaded with oil-in-water micro-emulsion and their properties were compared with these of an agar reference gel. Agar gels of concentration 2 % (w/v) were prepared by dissolving agar in Reverse Osmosis water. Each solution was heated over a hot plate in a Pyrex beaker placed in a bain-marie at 90 °C during 5 minutes. Then the agar dispersion was placed in an ice bath to rapidly cool down until a temperature of 40°C was reached. After that, the micro-emulsion was gradually added to the agar gel and the whole preparation was placed in the fridge. The agar reference gel without micro-emulsion was prepared using the same procedure. The composition of the gels is given in Table 2. To evaluate the maximum amount of micro-emulsion that could be loaded in the gel structure before detecting any phase separation, several agar gels were prepared (by mixing) with different concentration of micro-emulsion from 10 to 40 % w/v.

Table 2 Composition of agar gels (% weight)

<table>
<thead>
<tr>
<th>Gel</th>
<th>Agar</th>
<th>RO water</th>
<th>μE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ref</td>
<td>2</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>Gel1</td>
<td>2</td>
<td>88</td>
<td>10</td>
</tr>
<tr>
<td>Gel2</td>
<td>2</td>
<td>78</td>
<td>20</td>
</tr>
<tr>
<td>Gel3</td>
<td>2</td>
<td>68</td>
<td>30</td>
</tr>
<tr>
<td>Gel4</td>
<td>2</td>
<td>58</td>
<td>40</td>
</tr>
</tbody>
</table>
Preparation of the samples

The agar-micro-emulsion gels were used to clean the surface of wood samples (1,5 x 5 x 0,5 cm\(^3\)). This material was selected because of its porosity, allowing the trapping of materials into the structure. Bees wax was chosen due to its common use in conservation treatments and its solubility in hydrocarbon solvents. The wax was heated and applied on the samples with a brush and then with a spatula in order to increase its penetration into the porous matrix. The excess of wax was removed with only a thin layer of wax remaining on the samples. The cleaning test was performed by direct application of the reference gel and gels 1, 2, and 3 onto the area to be cleaned. The gels were stored during 24 hours before being applied on the samples. Each gel was applied during 90 minutes on the samples.

Results

After adding the first drops of micro-emulsions in agar, the gels become milky and show a high viscosity

![Fig. 4 Partial opacity in the agar-micro-emulsion gel with respect to the agar-gel transparency](Image)

For the agar-micro-emulsion gels, the gelation process occurs few minutes after the addition of micro-emulsion. Gels 1 and 2 are homogeneous. Gel 3 shows a small quantity of solvent in excess while the agar gel and the micro-emulsion are fully separated in gel 4. After 1 day of storage, the gels 1, 2 and 3 exhibit a small amount of solvent in excess, a
change of volume and a good strength. Agar-micro-emulsion gels, unlike pure one, are partially opaque.

The capability of the gel to retain the micro-emulsion in its structure was studied using the dehydration curves. Three agar-oil-in-water micro-emulsion gels (1, 2 and 3), the agar reference gel and the micro-emulsion were stored at ambient conditions (temperature: 25°C, ± 1°C, and relative humidity: 46%, ± 2%), and the evolution of their weights was measured. The Figure 5 shows no differences between the reference and the agar-oil-in-water micro-emulsion gels, suggesting that the presence of the micro-emulsion does not affect the retention properties of the agar

For cleaning, after 90 minutes of time application of gels 1, 2 and 3, the surface seems to be partially free of wax. This observation was confirmed by the UV inspection.
Introduction of oil-in-water micro-emulsion in agar gel when the gel is already formed does not prevent the gelation process of agar. The gel network is able to maintain its structure until 1.5% weight of Petroleum ether. This is sufficient to dissolve bees wax due to the high extracting efficiency of micro-emulsion.

The physical properties of the Agar gels are good enough for a conservation work when the concentrations of micro-emulsion are between 10 and 30% but they should be applied on the object during a long time. Moreover, agar gel allows the micro-emulsions to flow on the porous surface and to wet it but maintains the micro-emulsion in its structure and prevents the formation of rings. Evaporation of the solvents is slowed down and the gels can be used for a long period.
NOTES

10. Correspondence with K. Holmberg.

RÉSUMÉS

Le système composé d’un gel d’agar-agar et d’une microémulsion présente plusieurs qualités pour extraire des matériaux hydrophobes de couches poreuses. Les propriétés rhéologiques de ce système sont adaptées à un usage en restauration et sont stables pendant plusieurs jours. Les gels permettent la solubilisation du matériau à l’aide de faible quantité de solvant, l’empêchent de créer des auréoles, permettent le contrôle de l’évaporation des solvants et ne laissent pas de résidus de gel dans les pores.

Agar gel loaded with micro-emulsion could be used to extract lipophilic materials from porous surfaces. The physical properties of the gels are good enough for a conservation work. They allow the micro-emulsion to flow on the porous surface and to wet it but maintain the micro-emulsion in its structure and prevent the formation of rings. The evaporation of the solvents is slowed down and the gels can be used during a long period.
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Keywords: agar, micro-emulsion, cleaning, porous surface, gel, residue, ring

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