



The degradation of wall paintings and stone: Specific ion effects



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ARTICLE INFO

Article history:

Received 2 February 2016

Received in revised form 17 June 2016

Accepted 21 June 2016

Available online 1 July 2016

Keywords:

Salts

Crystallization

Wall paintings

Conservation

Cultural heritage

ABSTRACT

Salts are ubiquitous both on the surface and in the porous network of works of art such as wall paintings and stone. Cyclic solubilization and crystallization takes place with fluctuating environmental conditions, inducing mechanical stress in the pores and the flaking of the artistic surface. The preventive conservation of precious cultural heritage would thus benefit from models able to describe quantitatively the behavior of electrolyte solutions. Besides the pore size distribution of the wall, cyclic crystallization depends on relative humidity and temperature. Whereas the behavior of single salts' solutions is known, that of mixed solutions (commonly found on artifacts) is still an open issue, owing to the specific interactions of counterions and coions. Classical theories of electrolytes need many fitting parameters to provide predictive and quantitative information, and research focuses on matching phenomenological set of rules with models that take into account quantum mechanical dispersion forces. Classical models have been used so far to describe the behavior of some mixed salts' solutions commonly found on murals and stone, in terms of their RH_{eq} , which is the relative humidity of air in equilibrium with the saturated solution. Results indicate that environmental conditions deemed safe in the presence of single salts, represent indeed a threat to artifacts in the presence of mixed solutions, with other deviations due to the fact that the crystallization of salts takes place within mesoporous networks. We hope that the reviewed results might contribute a stimulus for further reanalysis of the degradation of works of art, where the synergistic effect of counterions and coions are taken into account. Such interpretation of the artifacts' degradation has been so far overlooked in preservation studies.

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1. Introduction

Cultural heritage is crucial to improvement of society, as it conveys ideals and values that contribute both education and entertainment. Besides, the valorization of cultural heritage leads to economic benefits, impacting on tourism and job creation [1,2]. Yet, works of art are subjected to degradation through a multitude of physical and chemical processes owing to the action of light, temperature, water or aqueous solutions, microorganisms, and even wrong conservation interventions [3,4].

In this framework, science (in particular, colloid, soft matter and materials science) has a central role both in describing degradation processes and providing solutions to counteract the deterioration of artistic and historical objects [5–7]. A great deal of effort has been put into understanding the role of salts, which are unsurprisingly ubiquitous in the degradation of works of art [8,9]. During the natural aging and weathering of plasters, the cyclic dissolution and re-crystallization of salts within the plaster's porous matrix result in flaking and detachment of the surface layers, eventually leading to the loss of precious

artifacts (see Fig. 1). Both preventing salt formation and removing detrimental salts from the surface and the bulk of the works of art are central tasks that are hampered by the fact that several fundamental aspects in the physico-chemical behavior of the saline species found on works of art are still poorly understood. This reflects a knowledge gap of the specific effects of electrolytes in chemistry and biology [10]. In fact, interactions between ions in aqueous solutions are usually described only through classical theories of electrolytes that work quantitatively and predictively only when many fitting parameters are used [11]. Recently, theoretical research has focused on matching phenomenological set of rules (that explain qualitatively ion–ion and ion–surface site interactions) with models that take into account quantum mechanical dispersion forces, in order to provide a complete description of the specific ion effects on the behavior of aqueous solutions of salts [10].

The main purpose of this contribution is to shed some light on the detrimental crystallization processes that continuously occur within the porous network of plasters and stone. These phenomena depend on temperature and relative humidity fluctuations, which are commonly experienced by artifacts exposed both outdoors and (less frequently) indoors. Besides, added complexity is due to the fact that the crystallization of salts takes place within porous networks, and the pore size distribution has an effect on the crystallization pressure [12,13].

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Fig. 1. Effects of salts crystallization on the surface of works of art. (Top row) 17th century limestone works (Angera stone) from the Ca' Granda Palace in Milan (Italy) showing delamination induced by salts in outdoor environment. (Bottom row) Mesoamerican wall paintings recently discovered in tombs located near Puebla (Mexico), where salts efflorescence causes flaking of the surface.

The thermodynamics of binary systems (single-salt aqueous solutions) represents the general background for defining the best conservation conditions. However, this approach is not predictive of a variety of processes that usually occur in the real systems. In fact, stone and walls usually contain solutions of several salts, even at high concentration, and this originates some unexpected processes [14^{**}]. Research on this topic is far from being concluded.

Considering the importance of cultural heritage conservation in our society, we have been solicited by the editors of this special issue to focus, in this contribution, on processes related to the degradation of works of art that might be associated to the synergistic effect of counterions and coions, although not strictly related to the Hofmeister effects. Such interpretation of the artifacts' degradation has been overlooked in conservation science; therefore we hope that this simple review might contribute a stimulus for further investigation and for a reanalysis of the degradation of works of art.

Namely, we will try to highlight trends in the behavior of the electrolytes in terms of differential (specific ion) effects on the equilibrium relative humidity (RH_{eq}), i.e. the relative humidity of air in equilibrium with a saturated solution of the salt. The knowledge of RH_{eq} for different salts is critical in preventive conservation, as it allows minimizing the cyclic crystallization of salts in the artifacts' pores. The RH_{eq} values for single salts are well known, however the behavior of mixed salts solutions is much more complex.

2. Single salt solutions: crystallization and relative humidity

As anticipated above, the environmental relative humidity (RH) plays a fundamental role in the salt crystallization process within porous stone. RH is defined as the ratio between the environmental air pressure and the saturation pressure, at a constant temperature. For air in equilibrium with a saline solution, RH is less than 100%, and the higher the concentration of the salt, the lower the RH. This is due to the fact that, within the solution, water molecules interact strongly with the dissolved ions, thus they exhibit a decrease tendency to

evaporate. That is to say, a saline solution has a value of saturated vapor pressure lower than that of pure water. When the saline solution is saturated, the RH of the air in equilibrium with the solution reaches a lower limit (the equilibrium relative humidity, RH_{eq}), whose value for some common salts is resumed in Table 1.

Dilute salt solutions typically impregnate porous walls or stone (see Section 3); upon gradual decrease of environmental RH water will evaporate and the solution's concentration will increase. In most cases, the surface of artifacts is always not in equilibrium, but the RH_{eq} values can be taken as useful parameters to predict what happens upon oscillations around the equilibrium. When the environmental RH equals RH_{eq} , the saline solution is saturated, and any further reduction of RH will cause evaporation of water and salt crystallization. If RH increases, the salt crystals adsorb water from the air, and form again solutions. In practice, artifacts commonly experience fluctuating RH both outdoors and indoors, which causes repeated crystallization of salts in the

Table 1

Equilibrium relative humidity (RH_{eq} %) and solubility (mol/L), at 20 °C, of salts that are commonly found in the pores of stone and wall paintings.

Salt	RH_{eq} (%)	Solubility (mol/L)
Ammonium nitrate	66	23.987
Sodium nitrate	75	10.836
Magnesium nitrate	53	8.428
Calcium nitrate	56	7.386
Ammonium chloride	80	6.955
Calcium chloride	33	6.713
Sodium chloride	75	6.143
Ammonium sulfate	81	5.826
Magnesium chloride	34	5.703
Potassium chloride	85	4.561
Potassium nitrate	94	3.264
Magnesium sulfate	90	2.916
Sodium sulfate	93	1.119
Potassium sulfate	98	0.689
Calcium sulfate	99.9	0.014

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