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Original article

Artwork conservation materials and Hansen solubility parameters: A novel methodology towards critical solvent selection



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ABSTRACT

In research and in actual conservation practice, conservators have to choose adequate methodologies for carrying out treatments successfully, while respecting the integrity of artworks. Besides the knowledge of the authentic materials present in each artwork, conservators must be able to choose appropriate conservation materials and methods. Solvents are widely used in cleaning, but solubility issues are also of high importance in consolidation treatments as well as in protective coating applications. The central aim of this work is to critically re-assess the potential of Hansen solubility parameters (HSPs) for a reliable use in the field of artwork conservation. An effort was made to develop an efficient methodology for critical solvent selection (CSS). For this purpose, two different methods were used for the estimation of various artwork conservation materials. A group-contribution method (GC), based on the chemical composition of materials, was applied for the prediction of HSPs of egg yolk, pine resin and seven red organic colorants (Mexican, Polish and Armenian cochineal, kermes, madder, lac dye and dragon's blood), traditionally used in paintings, textiles and illuminated manuscripts. Additionally, an experimental set up was used for testing the solubility of the commercial products of synthetic conservation materials, Primal AC-532K, Beva gel 371 a and b (old and new formula) and a commercial matt varnish made of dammar and wax. With the direct use of Hansen solubility parameters and the relative energy difference (RED) between various materials it was made possible to carry out *ad hoc* "virtual" solubility tests that may apply to real and complex systems such as cultural heritage artworks.

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1. Research aims

The aim of this research is to critically re-assess the use of Hansen solubility parameters (HSPs) and their potential application in the field of artwork conservation. For this reason, a set of materials was chosen, including binding media, protective coatings, adhesives and consolidants, and their partial solubility parameters were estimated using two different methods. The first one is a group-contribution method (GC), which is based on the chemical composition of materials. The second one is experimental, based on solubility tests with a set of solvents and mixtures. Using these two complementary methods, it was possible to supplement the existing databases for HSP of art and conservation materials ([supplementary material](#)). Furthermore, a novel methodology is proposed for critical solvent selection (CSS), with the direct use of HSPs and the relative energy difference (RED) between various art

and conservation materials. Through the proposed methodology it is possible to carry out *ad hoc* "virtual" solubility tests in order to facilitate hands on laboratory conservation practice and bring new perspectives in the treatment of complex and often multi-layered structures, like the cultural heritage artworks.

2. Introduction

In the field of cultural heritage conservation or conservation science, solvents and solvent formulations are widely used in the context of academic research as well as in the conservator's studio practice. Thus, the concept of solubility, the judicious selection of the appropriate solvent for the specific solute, and the use of rational solvent selection schemes, such as the partial or Hansen solubility parameters (HSPs), are particularly prominent. Since the theoretical background of the partial solubility parameters has been extensively discussed elsewhere [1,2], a brief mention of the relevant basics will be made here.

The starting point of the solubility parameter approach is due to Hildebrand [3], who introduced the total solubility parameter δ_{tot} ,

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or cohesive energy density (CED), as the square root of the ratio of the molar cohesion or potential energy, E_{coh} over the molar volume V :

$$\delta_{tot} \text{ (CED)} = \sqrt{\frac{E_{coh}}{V}} \quad (1)$$

In other words, the cohesive energy density is the total energy required to eliminate all intermolecular forces that keep molecules together and, as such, the following equation has been suggested for vaporizable compounds:

$$E_{coh} = \Delta H_{vap} + RT \quad (2)$$

where, ΔH_{vap} is the molar enthalpy of vaporization at temperature T . Combining equations (1) and (2), we get the following alternative definition of total solubility parameter:

$$\delta_{tot} = \sqrt{\frac{\Delta H_{vap} + RT}{V}} \quad (3)$$

Hansen [1,2], in the effort of improving the applicability of the total solubility parameter to compounds whose cohesive energy derives from dispersive forces but also polar and hydrogen-bonding forces, has divided the Hildebrand total solubility parameter into three partial components δ_d , δ_p and δ_{hb} , respectively. The sum of squares of these three partial components is the total solubility parameter, or:

$$\delta_{tot} = \sqrt{\delta_d^2 + \delta_p^2 + \delta_{hb}^2} \quad (4)$$

An alternative scheme was developed by Teas in 1968 [4], who used fractional parameters derived from the Hansen solubility parameters, as shown by the following equations:

$$f_d = \frac{\delta_d}{(\delta_d + \delta_p + \delta_{hb})} \quad (5)$$

$$f_p = \frac{\delta_p}{(\delta_d + \delta_p + \delta_{hb})} \quad (6)$$

$$f_{hb} = \frac{\delta_{hb}}{(\delta_d + \delta_p + \delta_{hb})} \quad (7)$$

and

$$f_d + f_p + f_{hb} = 1 \quad (8)$$

The partial solubility parameters of solvent mixtures can be easily obtained by calculating their mole fraction averages. This applies for both Hansen and Teas or fractional solubility parameters.

For the visualization of solubility data, two different systems exist: a two-dimensional (triangular) representation scheme or Teas chart, developed by Teas [4], and a three dimensional (solubility sphere) scheme as found in reference [5] and in [1,2]. In the first one, all solvents may be accommodated in a triangular graph as spots, on the basis of equations equations 5 to 8. Based on experimental data, the solubility windows of materials may be produced as contours embracing certain “good” solvents while excluding some “bad” others. The second system is a 3D representation and every solute – target is considered as a sphere, whose center is defined by its δ_d , δ_p and δ_{hb} values. The radius of the sphere, R_o , is the “interaction” radius considered to embrace the “good” solvents and exclude the “bad” ones. Of course, this method of depiction can also be reduced to 2D plots of cross-sections through the center of the solubility sphere on a graph perpendicular to each axis and resulting in three two-dimensional graphs [5]. Coming back to the 3D representation, the distance between the solute and any

solvent – or more generally, between any two materials – is given, R_a , the solubility parameter distance

$$R_a^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{hb1} - \delta_{hb2})^2 \quad (9)$$

where 1 and 2 refer to the solute and the solvent respectively, or any two different materials under study. The smaller the R_a , the better is the solvent for the solute. Another very useful parameter is the RED number, or the relative energy difference, given by the equation:

$$RED = R_a/R_o \quad (10)$$

R_o equals to the maximum value of R_a that still gives a “good” solvent.

RED becomes 0, if there is no energy difference. RED numbers less than 1.0 indicate high cohesive energy affinity, while progressively higher RED numbers indicate less effective solvents for the particular solute or target. The radius of a solute's sphere is defined through experimental solubility results from tests with a large number of solvents [1,2,5,6].

There is plenty of literature dedicated to the use of solubility parameters with relevant applications in the field of cultural heritage. These have focused mainly to the use of Teas chart, the fractional parameters concentrating, mainly, on varnish removal from painted artworks [7–15]. Coladonato and Scarpitti developed a software application called “interactive triangle of solvent and solubility triangle”, through which it is possible to plot Teas graphs for several art and conservation materials and get their solubility windows [16]. The Teas chart system was criticized for its limitations and inaccuracy [5,17,18]. More recently, the direct use the Hansen solubility parameters was discussed in the field of artwork conservation [19,20].

The present work reports the first results of a research study that was carried out regarding the solubility of art and conservation materials. The focus is on the direct use of the Hansen solubility parameters and the possibility to carry out *ad hoc* “virtual” solubility tests for the removal or application of conservation materials, paying attention to the safety of original constitutive materials of the artwork as well as the safety of the conservator.

3. Materials and methods

3.1. HSP estimation methods

3.1.1. Group-contribution method

The group-contribution method is computational/theoretical and no experimental data is needed, besides the molecular structure of the materials, in order to calculate their partial solubility parameters. The description of the molecular structure is done using two kinds of functional groups: the first-order groups, which are used to describe the basic molecular structure, and the second-order groups that are based on the conjugation theory [21]. The latter groups are based on the ABC framework, developed by Mavrouniotis et al. [22]. The basic equation for calculating the property values, as derived from the molecular structure of a given molecular structure is the following:

$$f(x) = \sum_i N_i C_i + W \sum_i M_j D_j \quad (\text{MPa})^{(1/2)} \quad (11)$$

where, C_i is the first-order group-contribution of type i appearing N_i times and D_j is the second-order group of type j appearing M_j times. W is a constant, which equals 0 if no second-order groups are found and 1 if any second-order groups are found in a given compound. The determination of the group-contributions is described

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