

The kinetics of dissolution of varnishes: The influence of vapour pressure on the rate of solvent action

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ABSTRACT

The kinetics of dissolution and rates of leaching were studied in relation to the surface cleaning of modern oil paint in art conservation. A wide range of materials of different polarity and molecular mass was tested to characterise the rate of dissolution. The large data set suggests that the rate of solvent action is mainly influenced by the physical properties of the solvent. The kinetics of dissolution are mainly controlled by the vapour pressure of the solvent, since the entropy change is strongly influenced by the cohesive energy of the liquid. The lower the molecular mass and polarity of the solute molecule, the more dominant is this effect. The same mechanism is relevant to describe the rate of leaching of low molecular weight material from aged oil paint. Generally, high vapour pressure solvents exhibit a more prominent leaching effect upon short-term interaction than similar solvents with a low vapour pressure.

INTRODUCTION

Effective and responsible use of solvents is an important competence of a conservator/restorer. The goal to selectively remove components such as varnishes from the surface without affecting underlying paint is a common challenge in the field of restoration. The complexity of the processes of solvation and dissolution has given rise to several approaches by various groups to simplify solvent action and deliver some selection criteria to the restorer. In general, however, these approaches lack both a qualitative and quantitative description of the dissolution processes. In the context of practical conservation needs, knowledge of the rate of solvent action will decide the ability to control a conservation treatment. Since the kinetics of solvent action mainly depend on an entropy change in the dissolving process, a different approach is necessary to satisfy the demands of current conservation practice.

Theory of dissolution

In the field of solvent chemistry, different concepts based on the fundamental principle of thermodynamics are used to describe the process of mixing. Essentially solvent–solute mixing may be characterised by the change in the Gibbs energy of a system:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

The enthalpy of mixing ΔH_m , which corresponds to the commonly known rule of ‘like dissolves like’, reflects the strength of the intermolecular interactions (Reichardt 1990). Based on the second law of thermodynamics, the entropy of mixing ΔS_m at a given temperature T is the driving force and is thus of high relevance to the description of the solubility of a material. This value is a measure of the disordering of a system and describes the distribution of the solid molecules into the surrounding liquid. The change in entropy is therefore largely dependent on the strength of the intermolecular interactions within the liquid, because the liquid cohesion has to be overcome first to create space or a ‘cavity’ in the liquid prior to incorporating the solute (Chipperfield 1999). This energetic process is visualised in Figure 1.

Since dissolution is influenced by the intermolecular interactions between solvent and solute, as well as the liquid properties of the solvent itself, both aspects need to be accounted for. To describe the solvent sensitivity

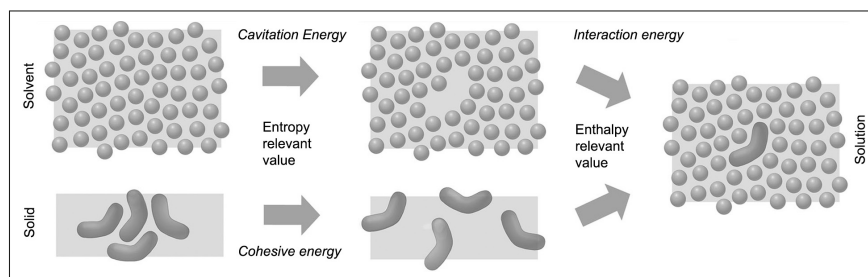


Figure 1

Energetic scheme of dissolution. The endo-energetic cavitation energy influences the entropy of mixing, while the interaction energy describes the enthalpy of mixing with a specific solute

of a material, the swelling behaviour of different modern artist paints was investigated. Based on this data, a graphical solvent action parametrisation scheme was developed in previous work (Zumbühl 2014). This system combines relevant parameters for the solvent action to characterise the solvation and dissolution properties of different binding media. It interconnects different concepts used in solvent chemistry and is based on the normalised and material-dependent solubility parameter. In the graphical scheme, the solvents were divided into six subgroups based on their interaction and structural characteristics to improve the specificity of the system. In its present form, the developed scheme provides information on the swelling properties of artist paints (Figure 2). However, in applying this system to varnish materials, it was not possible to visualise the dissolution behaviour in a systematic way. This implies that the process of dissolution is not dominated only by intermolecular interaction. From a theoretical point of view, the kinetics of dissolution should be strongly influenced by the ‘cavitation energy’ of the liquid phase. This entropy-relevant effect, including the effects of leaching upon short-term application of solvents, was investigated for a large variety of materials. The result is the addition of an important dimension to the system, which is of direct relevance to the practical application of solvents in conservation treatments.

EXPERIMENTAL

For the systematic description of the solvent action on solids, a wide range of materials of different polarity and molecular mass was tested with a large variety of solvents with characteristic interaction properties. The swelling behaviour of 7 paint systems was assessed according the principle by Phenix (2002). The dissolution properties of 14 binder and varnish materials were quantified according to the method by Engel (2011). Each of these materials was tested using a set of 50 solvents (Merck). The focus in this paper is the solvent sensitivity of varnish materials. The low molecular weight binder and varnish materials tested were: fresh and aged dammar (Kremer), fresh and light aged (indoor condition, 5 years) (MS2A resin BASF), as well as Regalrez 1094 (Regalite R1100) (Eastman), Kristalex 3070 (Kristalex F85) (Eastman) and Laropal A81 (BASF). Other tested polymeric materials were Aquazol 500 (Performance Chemicals ISP), Mowilith 20 (Hoechst), Mowiol 4-88 (Kuraray), Paraloid B-72 (Roehm&Haas), Degalan PQ611 (Roehm&Haas), Schmincke Colloidal Varnish (Schmincke) and Golden Polymer Varnish (Engel 2011). In order to obtain a standardised testing method, the binding agents were ground in a

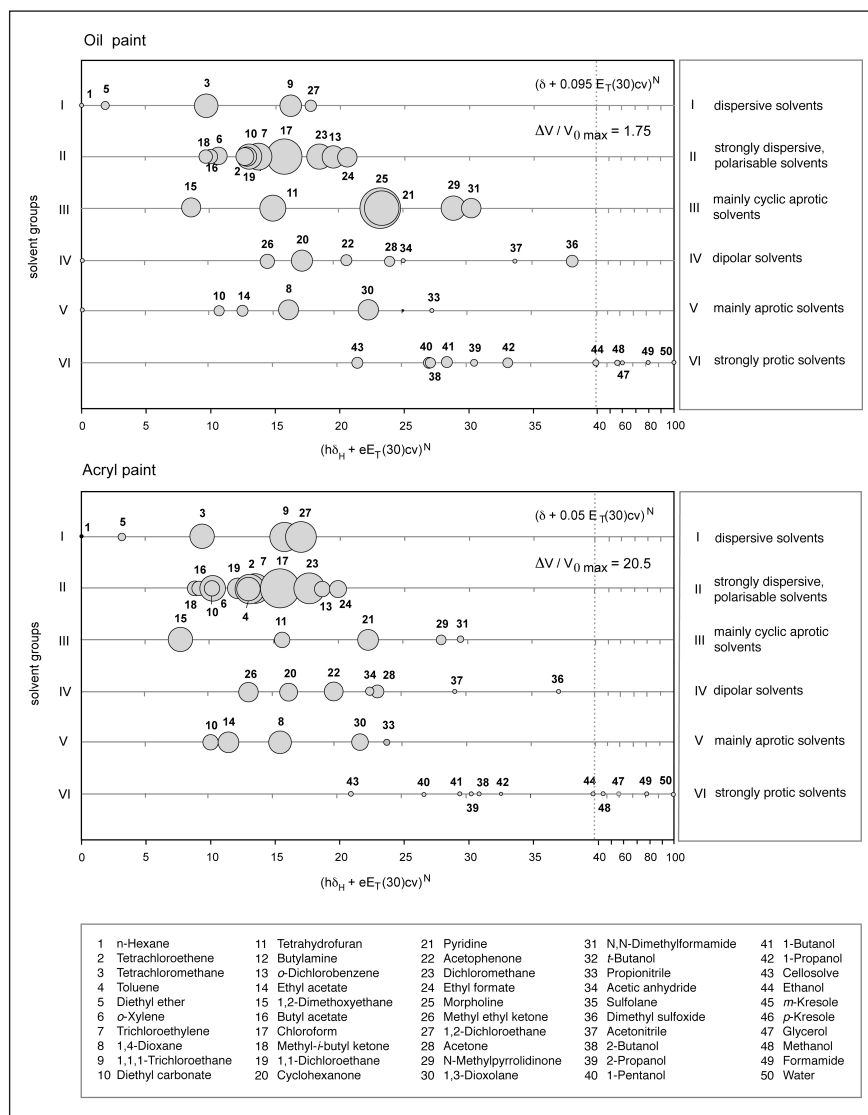


Figure 2

Plot of solvent action representing the swelling capacity of solvents on oil (upper) and acrylic paint (lower). The normalised swelling values of the solvents are displayed as variably sized circles, whereby the diameter corresponds to the intensity of action of the different solvents relative to the solvent with the highest swelling action

mortar and pressed to pellets of $\varnothing 0.5$ mm and the same weight ($\pm 10\%$). The rate of dissolution was determined under a saturated solvent gas atmosphere (Engel 2011). Leachate quantification was performed on Norma Oil colour films containing bone black PBk9 (Schmincke). Leaching experiments were run on aged films made of linseed oil paint with free fatty acids, lead white PW4 (Kremer), and an additive content of 5% (relative to the amount of oil) with stearic acid (Merck) and azealic acid (Merck). All paint was applied at a film thickness of 300 μm with a Film Applicator Model 360 (Erichsen) on a silicon-coated Hostaphan-Foil RNT 36 (Kremer) and pre-dried in darkness under room conditions (23°C/50% RH) for 7 days. The samples were aged under window-glass-filtered fluorescence light (True Lite 5500K and Philips UV-20W/08 F20 T12 BLB generating ≈ 5800 lm/m^2 , 557 mW/lm^{-1} / ≈ 3200 mW/m^2) at $\approx 40^\circ\text{C}$, 55% RH and atmospheric oxygen content over a time period of 6 weeks. For the quantification of the leachable components, paint samples of 1 cm^2 (average weight $\pm 4\%$) were immersed in solvent for 5, 10, 20 and 30 seconds and then dried for 7 days. Gravimetric measurements (quantification of the weight loss of the

paint) were run on a Mettler MT5 scale (accuracy: 0.001 mg). The leached material was characterised using Fourier transform infrared spectroscopy (FTIR) and electrospray ionisation mass spectrometry (ESI-MS).

RESULTS AND DISCUSSION

While solvent exposure is commonly limited and minimised, knowledge of the rate of dissolution is of decisive relevance to applications in art conservation with short interaction times. In this respect one should note that an increased intermolecular interaction between the solvent and the material does not necessarily lead to better solubility. It was observed that the swelling of paints is greatest when the interaction with the solute is high, while the interaction within the solvent is low (Zumbühl 2014). Generally, the kinetics of dissolution is strongly influenced by the cohesive energy of a solvent or solvent mixture, since this liquid property has a great influence on the entropy of dissolution. This means that the lower the cohesive energy of the solvent, the better the dispersion of the solid molecules into the surrounding liquid. In this context, this liquid property is to be regarded as the activation barrier of dissolution. In other words, the solvent's vapour pressure can be regarded as an indicator for the solubility rate. Taking this additional dimension into account (in hPa (25°C), along x), this new system graphically combines solubility characteristics (solvent groups I–VI according to Figure 1) with information on the rate of dissolution (diameter of symbol) of selected material systems (separate plots). The data is split into solvent groups for better differentiation of the specific solvent properties, as well as greater readability of the graphic system. The interaction properties were classified using the solvatochromic LSER-interaction parameter values introduced by Kamlet and Taft (Kamlet and Taft 1985, Marcus 1998). This concept parameterises solvents, based on the individual scales of different intermolecular interactions. A linear dependence on these solvent parameters is used to correlate the rate of individual reactions and the prediction of a wide variety of solvent effects. Further differentiation is based on the polarisability and the dipole moment of the solvent molecules, as well as the cohesive energy of these liquids and the molecular structure (Marcus 1998), as described elsewhere (Zumbühl 2014).

The kinetics of dissolution of varnish materials

The solubility of a material depends, in principle, on the interaction properties and its molecular mass. This has necessitated the analysis of a wide range of varnish materials to achieve a representative coverage. The results unravelled a broad spectrum of solubility for most of the common varnish materials, extending across multiple solvent classes (groups I–VI). Furthermore, there is an observed trend of an increasing rate of dissolution correlating with higher vapour pressures within the solvent groups. The rate of dissolution of low molecular materials (< 2000 Da) is thus dominantly influenced by the solvent's vapour pressure. Variable polarity across the materials, however, limits the solubility range. As a result it can be observed that apolar hydrocarbon resins are only soluble in dispersive solvents of groups I and II, whereas the aldehyde resin Laropal A81 can be solved in aprotic and dipolar solvents (Figure 3).

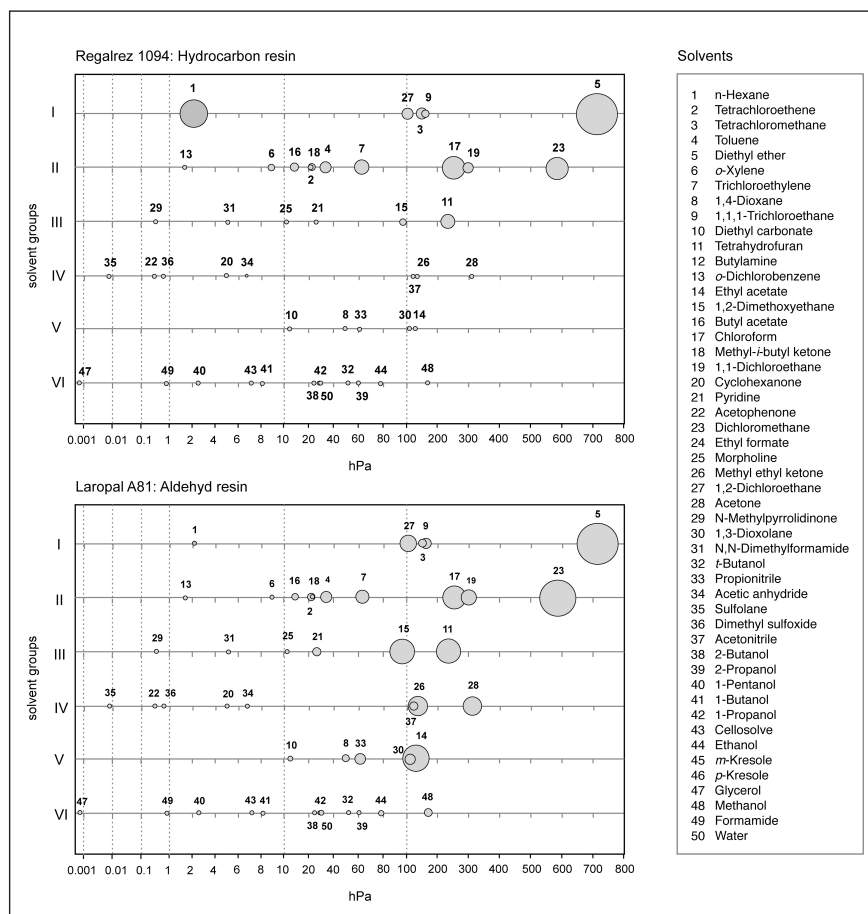


Figure 3

Solubility plot of the low-molecular-weight varnish materials Regalrez 1094 (upper) and Laropal A81 (lower). The rate of solubility normalised to the fastest acting solvent is displayed as variably sized circles, whereby the diameter corresponds to the relative intensity of action of the different solvents

Both attractive forces and repulsive forces within the liquid play an important role in the process of dissolution of a material (Zumbühl 2014). This applies to ethers and ketones, both of which have low cohesive energies. Thus, vapour pressure controls dissolution independently of the polarity of a system. This is also true for aged varnishes undergoing strong oxidation. While the solubility range shifts towards the polar solvent groups, the rate of dissolution remains vapour pressure dependent within the solvent group (Figure 4). The solubility of high molecular varnish materials (> 100 kDa) such as acrylics presents a similar picture, even though interaction properties play a slightly more relevant role. This is particularly the case with the weakly dispersive solvents of group I, having virtually no effect (Figure 5). The dominance of the vapour pressure on dissolution kinetics was confirmed across a broad spectrum of varnish materials. Based on experimental observations, we can state that the rate of dissolution of all tested varnish materials is strongly accelerated at vapour pressures exceeding > 100 hPa (25°C). These data prove the dominant influence of the cohesive energy of the solvent as an entropy-relevant factor on the kinetics of dissolution.

The kinetics of leaching in oil paint

Within the context of varnish solubility, it is necessary to elucidate the detrimental action of solvents on underlying paint layers. Over the last

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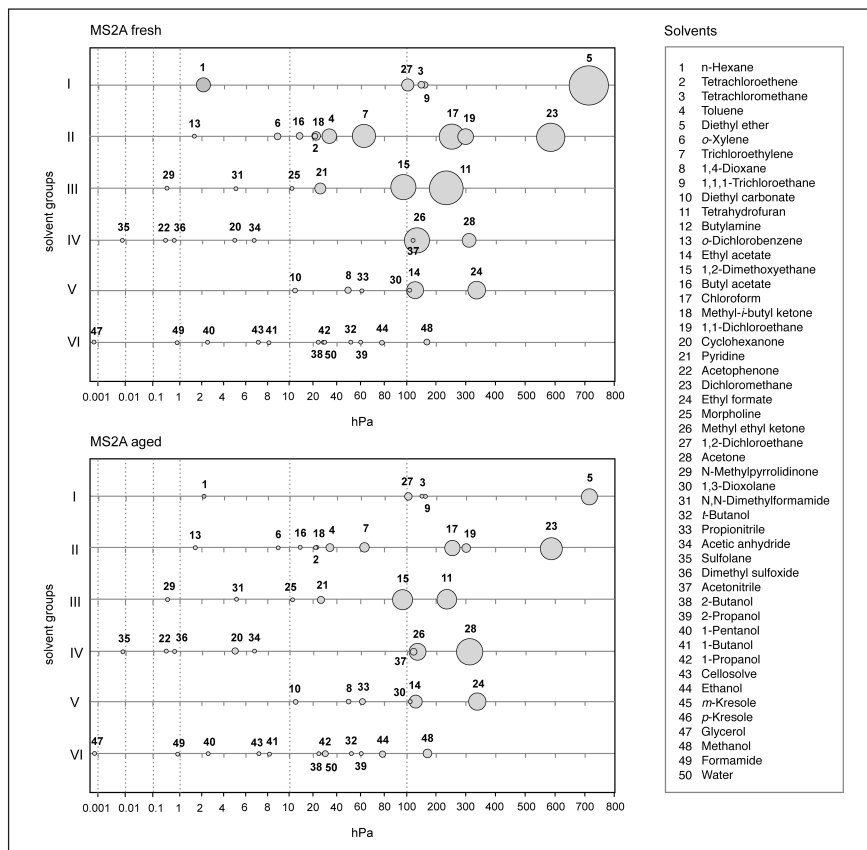


Figure 4

Solubility plot of fresh (upper) and aged (lower) ketone resin MS2A. The rate of solubility normalised to the fastest acting solvent is displayed as variably sized circles, whereby the diameter corresponds to the relative intensity of action of the different solvents

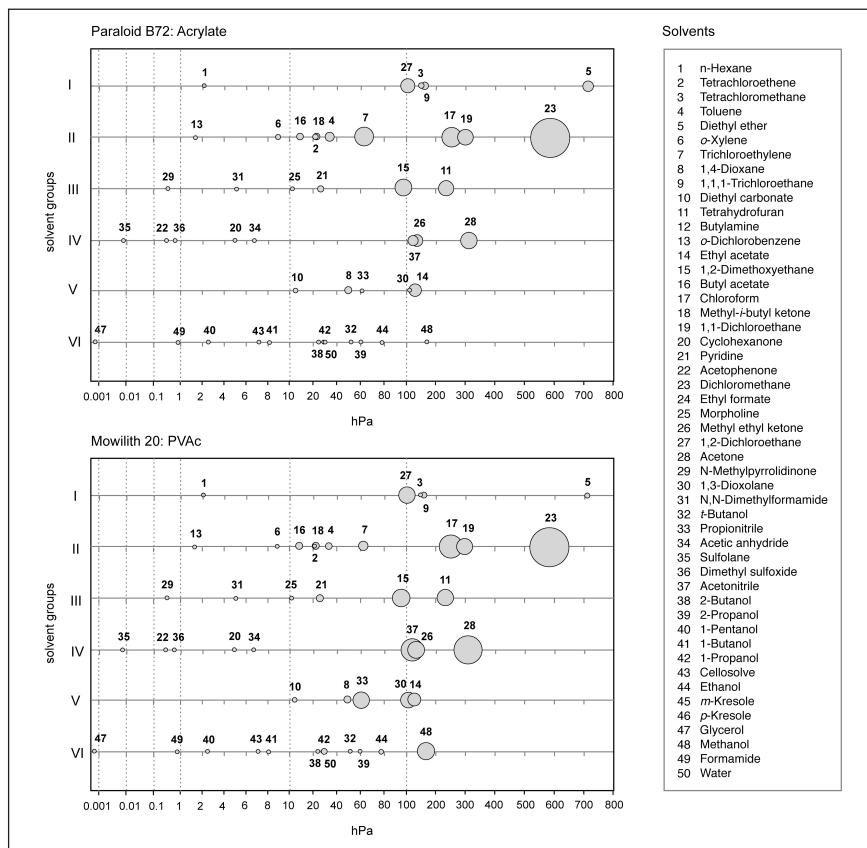


Figure 5

Solubility plot of the high-molecular-weight polymers Paraloid B-72 (upper) and Mowilith 20 (lower). The rate of solubility normalised to the fastest acting solvent is displayed as variably sized circles, whereby the diameter corresponds to the relative intensity of action of the different solvents

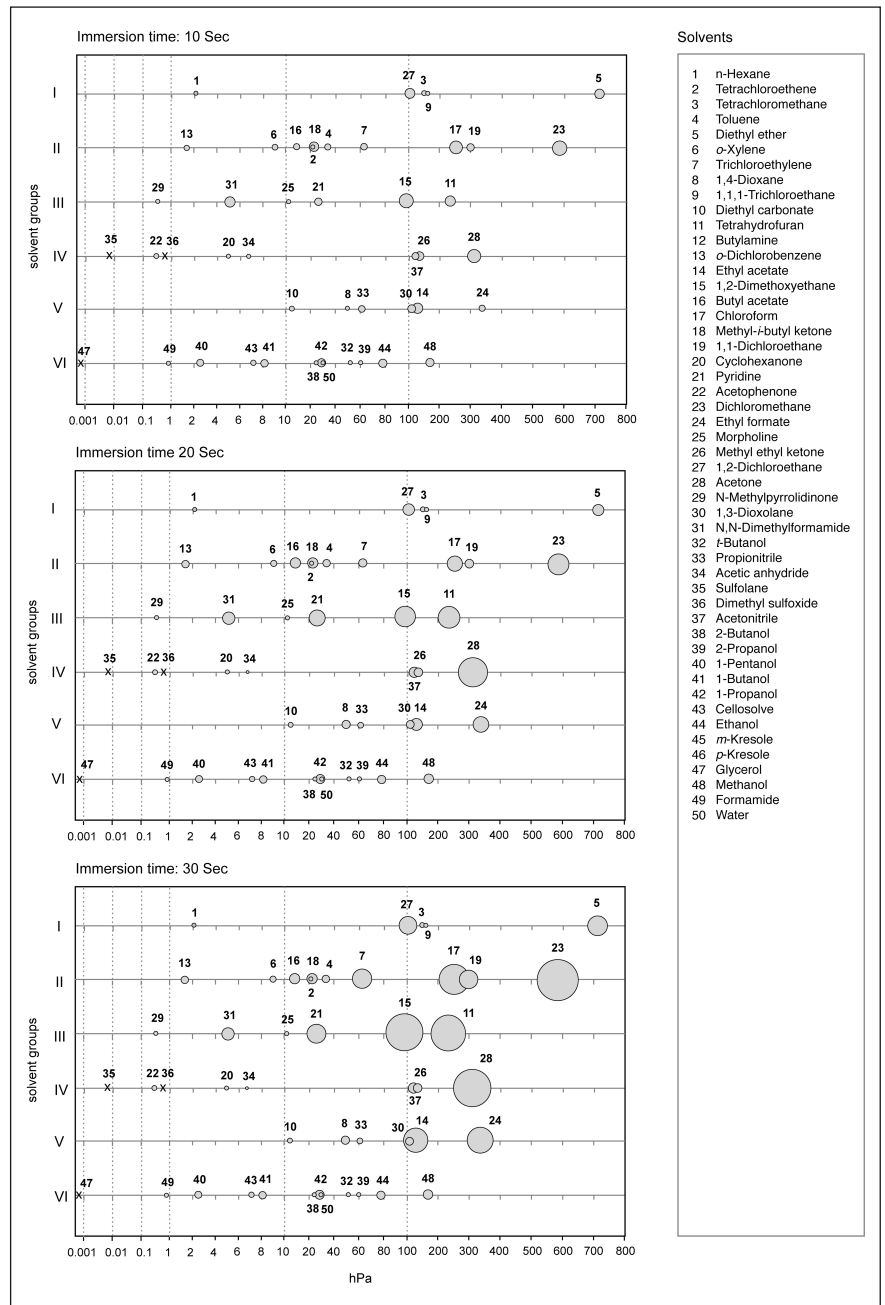


Figure 6

Leaching plot of aged oil paint representing the rate of leaching normalised to the solvent with the highest action (after 30 sec). The variably sized circles represent the quantitative leaching capacity after 10 sec (upper), 20 sec (middle) and 30 sec (lower) immersion time

few years, this type of research has focused on the total leaching of low molecular additives and several ageing products by long-term immersion in solvents (Sutherland 1999). Our paper now adds data on the kinetics of this process. Leaching of paint components was quantified gravimetrically on paint film samples of a commercial oil paint after accelerated ageing. Measurements were performed after short immersion times of 5, 10, 20 and 30 seconds. These experiments focus on the leaching of paint components within the first few seconds of interaction. In the presented case, the initially leached compounds were primarily oxidised triglyceride fragments. The data documents that leaching of paint layer components strongly depends on the physical properties of the solvent. As previously discussed, the rate of dissolution was strongly controlled by the vapour pressure (Figure 6). Overall, these experiments revealed the severely detrimental effect of

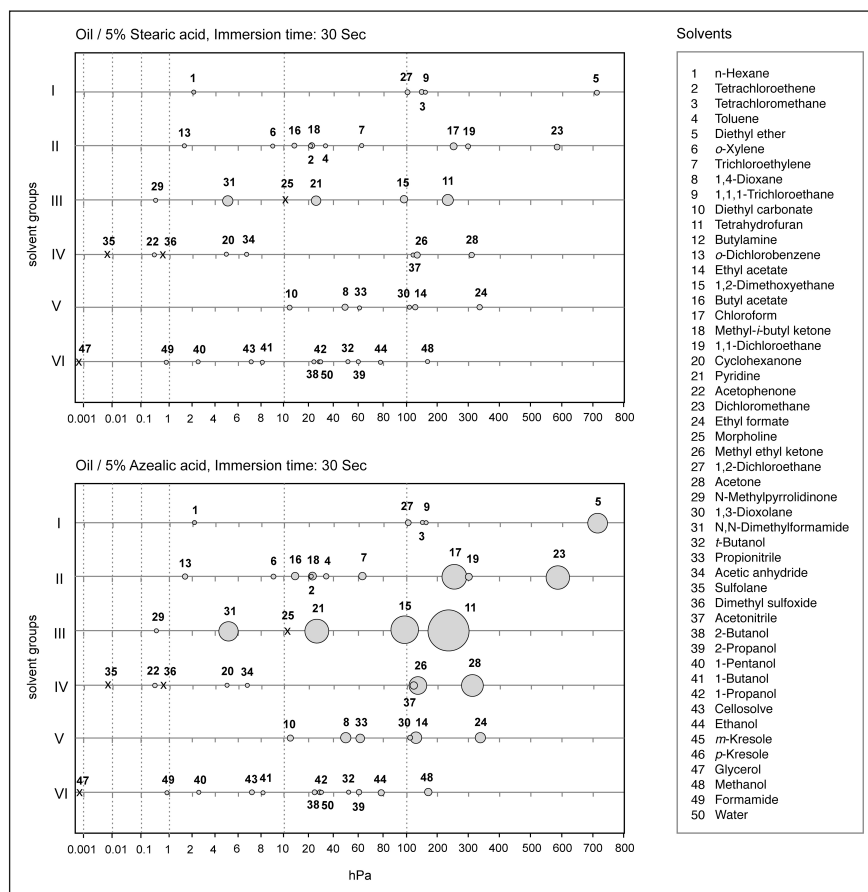


Figure 7

Leaching plot of aged oil paint representing the rate of leaching of stearic acid (upper) and azelaic acid (lower) after 30 sec immersion time. The variably sized circles represent the quantitative leaching capacity relative to the solvent with the highest action

all solvents exhibiting high vapour pressures across the different solvent groups I–VI. Furthermore, the specific leachability of the free fatty acids and the dicarboxylic acids as common degradation products in oil paint was explored. Both compounds were leached mainly in aprotic solvents with highly dispersive interaction properties from group III. Differences are seen in the relative quantities leached. Due to the low molecular mass and the two protic groups, azelaic acid is more easily leached than stearic acid (Figure 7). The strong correlation between the rate of dissolution and vapour pressure was confirmed once more.

Influence of the vapour pressure on the rate of solvent action

Based on the large data set available, it is possible to derive general information on the material solubility. The influence of the vapour pressure of the solvent – or of a solvent mixture – on the rate of dissolution is clearly evident. The lower the molecular mass of the solute molecule, the more dominant is the effect. In all experiment series, the solvent's vapour pressure had a decisive influence on the rate of solvent action. The kinetics of the solubility of a material therefore does not primarily depend on the intermolecular interaction, but is essentially driven by the physical properties of the solvent. Quantitative results derived from long-term experiments can thus not be compared with the time-resolved short-term experiments of this research, chosen to reflect the practical situation of a restorer. The current data set indicates that the cavitation

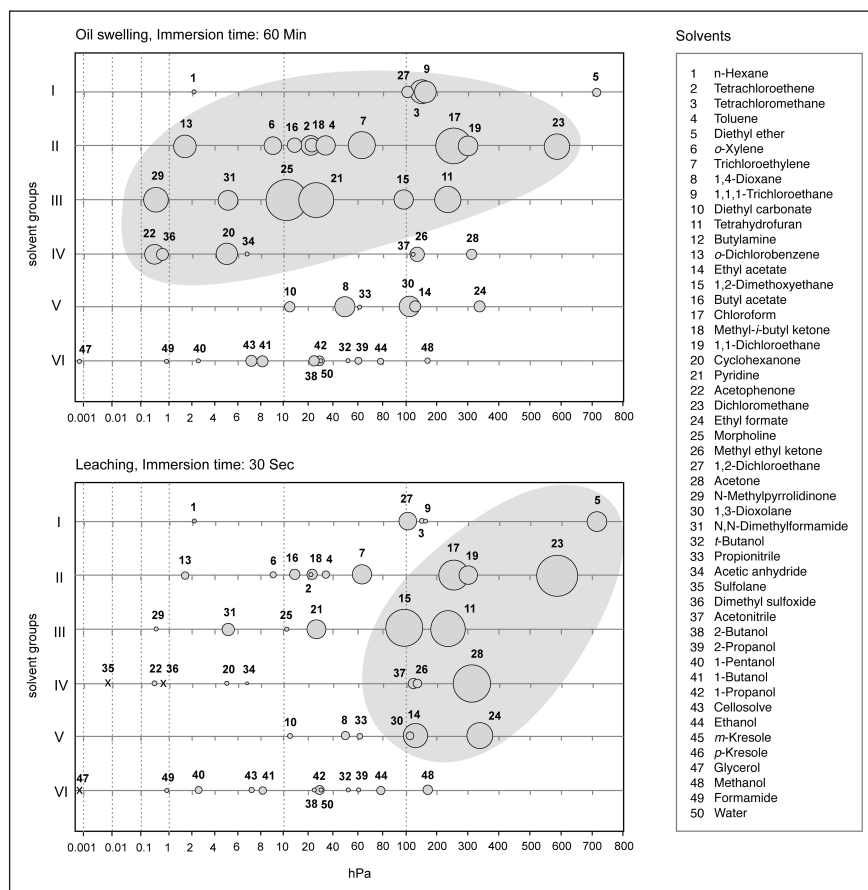


Figure 8

Swelling (upper) and leaching plot after 30 sec immersion time (lower) of aged oil paint. The variably sized circles represent the rate of action normalised to the solvent with the highest action. The plot illustrates that the rate of leaching after the short-term action of solvents is not influenced by the potential swelling capacity of the material

energy (cohesive energy of the solvent) is a rate-controlling factor in the dissolution of all varnish materials tested. This is due to the fact that, with the low cohesive energy of the liquid, less energy is required to disperse a solute molecule into the solvent and achieve a high rate of mixing. Thus, the change in the entropy of dissolution is generally high in solvents with high vapour pressure. Parallel to this improved solubility of varnish materials, however, there is an increased leaching of underlying paint compounds. Apart from the dissolution effect mentioned above, this is partly also due to the rate of swelling of the paint layer. Thus, a decisive observation within this data set is the fact that high vapour pressure solvents exhibit a more damaging effect after short-term interaction on paint than similar solvents with a low vapour pressure. The same effect was found in solvent mixtures (Zumbühl et al. 2013). This clearly contradicts the common belief in conservation practice that solvents with a high vapour pressure are less risky, as these would volatilise more rapidly. The rate of leaching during the short-term action of solvents was neither influenced by the potential swelling capacity of the material (Figure 8), nor by the retention of the solvent. In fact, the detrimental action by solvents is controlled by the speed of the different processes, including the dissolution kinetics as well as the time dependent rate of swelling. The results comply with observations made in previous studies, where solvents with high vapour pressures lead to more substantial modifications of the mechanical film

properties than all the remaining solvents (Fuesers and Zumbühl 2008, Zumbühl et al. 2008). These data highlight the utmost importance of incorporating kinetic aspects of solvent action into the solvent schemes that are used to implement sustainable conservation strategies.

CONCLUSION

A wide range of materials of different polarity and molecular mass was tested to characterise the kinetics of dissolution and leaching. The current data set suggests that the rate of solvent action is mainly influenced by the physical properties of the solvent. Intermolecular interaction between the solvent and solute is far less relevant than previously assumed. Particular attention within this context should be given to the influence of the solvent's vapour pressure on the rate of dissolution, due to the reduced cavitation energy of the solvent, which increases the entropy of dissolution. In all material/solvent combinations tested, the cavitation energy played a key role in the dissolution process. This means that the kinetics of dissolution is mainly influenced by the cohesive energy of the solvent or the solvent mixtures. The lower the molecular mass and polarity of the solute molecule, the more dominant is this effect. The same mechanism is also relevant to describe the rate of leaching. Generally, high vapour pressure solvents exhibit a more damaging effect after short-term interaction than do similar solvents with a lower vapour pressure. With respect to potential paint layer damage induced by conservation treatments, it is not only necessary to consider the time of interaction of the solvent during the working process; it is also essential to include the reaction kinetics of the solvent to arrive at a meaningful judgement. In conclusion, by keeping to short interaction times, solvents with lower vapour pressure will be less detrimental to paint layers than solvents with a high vapour pressure, since the dissolving rate of the leachate is reduced and the swelling of the paint layer proceeds at a lower pace.

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