

# The Kinetics of Dissolution of Varnishes: Influence of the Vapour Pressure on the Rate of Solvent Action

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## Introduction:

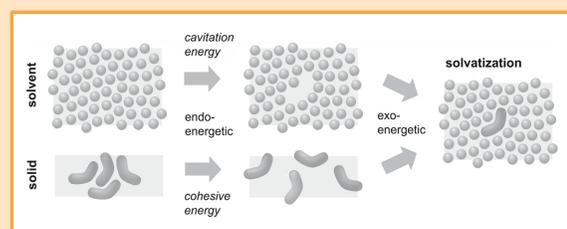
The kinetics of dissolution and rates of leaching were studied in relation to surface cleaning of modern oil paint in art conservation. A wide range of materials of different polarity and molecular mass was tested to characterise the rate of dissolution. The large data set suggests, that the rate of solvent action is mainly influenced by the physical properties of the solvent itself and not by the intermolecular interaction of the solvent with the solute molecules.

## Theory of dissolution:

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

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

The enthalpy of mixing  $\Delta H_m$ , which corresponds to the commonly known rule of “like dissolves like”, reflects the strength of the intermolecular interactions. Based on the second law of thermodynamics, the entropy of mixing  $\Delta S_m$  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. This energetic process is visualised in **Figure 1**. 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 taken as an indicator for the solubility rate.



**Figure 1:** Energetic scheme of dissolution. The endoenergetic cavitation energy influences the entropy of mixing, while the interaction energy describes the enthalpy of mixing with a specific solute.

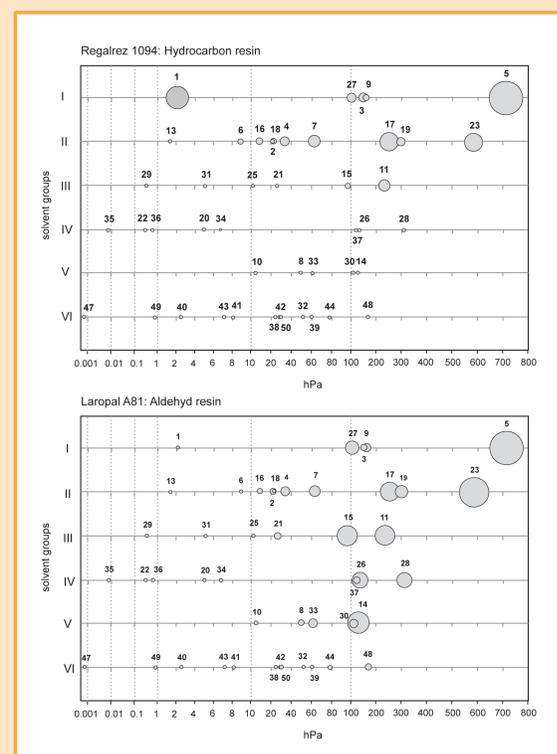
1	n-Hexane	26	Methyl ethyl ketone
2	Tetrachloroethene	27	1,2-Dichloroethane
3	Tetrachloromethane	28	Acetone
4	Toluene	29	N-Methylpyrrolidinone
5	Diethyl ether	30	1,3-Dioxolane
6	o-Xylene	31	N,N-Dimethylformamide
7	Trichloroethylene	32	t-Butanol
8	1,4-Dioxane	33	Propionitrile
9	1,1,1-Trichloroethane	34	Acetic anhydride
10	Diethyl carbonate	35	Sulfolane
11	Tetrahydrofuran	36	Dimethyl sulfoxide
12	Butylamine	37	Acetonitrile
13	o-Dichlorobenzene	38	2-Butanol
14	Ethyl acetate	39	2-Propanol
15	1,2-Dimethoxyethane	40	1-Pentanol
16	Butyl acetate	41	1-Butanol
17	Chloroform	42	1-Propanol
18	Methyl-i-butyl ketone	43	Cellosolve
19	1,1-Dichloroethane	44	Ethanol
20	Cyclohexanone	45	m-Kresole
21	Pyridine	46	p-Kresole
22	Acetophenone	47	Glycerol
23	Dichloromethane	48	Methanol
24	Ethyl formate	49	Formamide
25	Morpholine	50	Water

**Table 1:** Solvents used for solubility tests.

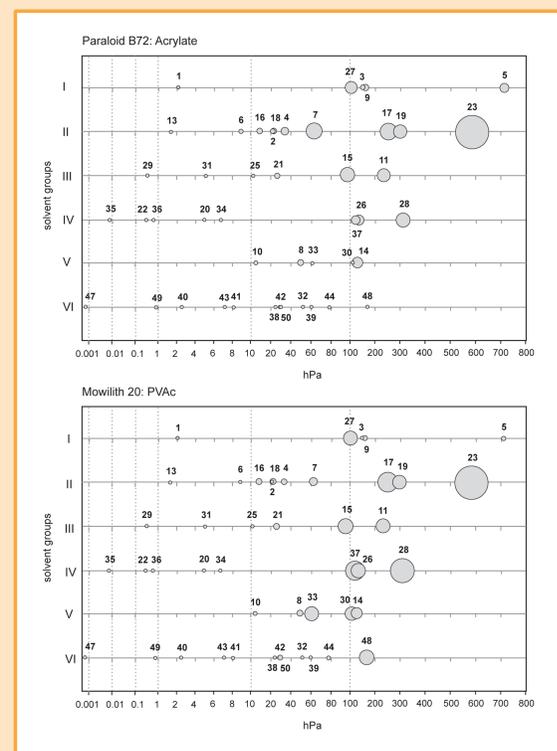
## Results and discussion:

The solubility of 14 binder and varnish materials of different polarity and molecular mass was tested in 50 solvents (**Table 1**). The current data set suggests, that the rate of solvent action is mainly influenced by 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 (**Figures 2 and 3**). This means that the kinetics of dissolution is mainly influenced by the cohesive energy of the solvents. The lower the molecular mass and polarity of the solute molecule, the more dominant is this effect.

Based on these results a new parametrisation system to describe the speed of solvent action was developed. 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 [1] for better differentiation of the specific solvent properties, as well as more readability of the graphic system.



**Figure 2:** Solubility plot of the low molecular weight varnish materials [2]. 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 3:** Solubility plot of the high molecular weight varnish materials [2]. The variably sized circles correspond to the relative intensity of action of the different solvents.

This is an excerpt of the full text publications below:

[1] Stefan Zumbühl, Parametrization of the Solvent Action on Modern Artists’ Paint Systems, Studies in Conservation 59-1 (2014) 24-37. 1611, 11 pages (2014).

[2] Stefan Zumbühl, Nadim C. Scherrer, Nina L. Engel, Wolfgang Müller, The Kinetics of Dissolution of Varnishes – The Influence of Vapour Pressure on the Rate of Solvent Action, ICOM-CC 17th Triennial Conference Preprints, Melbourne 15-19 September, J. Bridgland (Ed.), Art. 1611, 11 pages (2014).