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Cover image Micrograph of the surface of a Winsor & Newton Ultramarine tube paint after incubation with sulfur dioxide. See paper by Silvester et al. in this issue

Original research or treatment paper

Parametrization of the solvent action on modern artists' paint systems

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A solvent action parametrization scheme has been developed combining relevant parameters of the solvent action on modern artists' paints to characterize the solvation and dissolving properties of different binding media. The new system combines different concepts used in solvent chemistry. It is based on the normalized and solute-dependent dimension $[h\delta_H + eE_T(30)cv]^N$. It comprises a polarity value $E_T(30)cv$ as the magnitude of the enthalpy, and a combined value representing the cavitation energy δ_H as an entropy-influencing factor. Forty-eight solvents were divided into five subgroups based on their interaction and structural properties. This binary scheme permits to reliably quantify spaces of efficiency. The graphical selectivity of the scheme was applied to four binding media systems (oil, alkyd, acrylic-, and acrylic-polystyrene) by determination of the swelling capacity of 48 solvents. The graphical visualization of the systematic parametrization of solvents permits one to judge the intermolecular interaction and other effects of solvation relevant to the restoration of painted artwork.

Keywords: Solvent action, Parametrization, Modern paints, Cavitation energy, Linear salvation energy relationships, Swelling, Solvatisation, Solubilization

Introduction

Effective and responsible use of solvents is an essential skill of a conservator or restorer. The complexity of solvent processes in the field of conservation/restoration arises from the intent to selectively remove surficial components of a paint build-up without affecting underlying strata. High demands are thus set on the restorer/conservator with respect to specific knowledge on the dissolving properties of a wide range of materials. Owing to the complexity of the solvation and dissolving processes several approaches have been made to simplify solvent action and deliver some selection criteria to the restorer. The ternary 'Teas chart' (Teas, 1968) is the most widely applied solvent classification scheme in conservation (Torraca, 1978; Banik & Krist, 1984; Lorentz, 1998; Pietsch, 2002; Saera Vila & Barros Garcia, 2013), even though the system does not permit the prediction of material solubility. With the ternary Teas chart it is not possible to map the solvent action quantitatively (Phenix, 2002a, b, 2013; Zumbühl, 2005). This is due to the fact that the system ignores important intermolecular interactions. With this simplification, the relation of the individual parameters to the total strength of interaction forces is lost.

In addition, while this system describes the solvents' properties, it does not deliver information on material solubility. Yet, there is no doubt that a graphical tool would greatly assist the work of a conservator/restorer for the strategic and material-based selection of solvents. This paper aims at investigating the solvation properties (intermolecular interaction of the solvents with the solid material) as well as the relevant factors of the dissolving process (distribution of a solute molecule in the surrounding liquid). The solvation theory, however, describes qualitative reaction but delivers no information on the reaction rate of a process. Nevertheless, these results deliver important knowledge on the systematic description of a material solubility and as such form the first step towards the development of a parametrization scheme as a tool for restoration/conservation of painted artwork.

Theory of the dissolving process

There is a large number of parametrization systems available in the field of solvent chemistry (Hoy, 1975; Gardon & Teas, 1976; Gutmann, 1977; Barton, 1991; Reichardt, 1994; Nigam & Rutan, 2001; Wypach, 2001), as well as in industry (Hansen, 2000, 2007) and in art conservation (Phenix, 1998). One type classifies the solvent properties, whereas other models are used to describe the processes of solvation (Oakey & Morokuma, 1975;

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Christenson & Horn, 1985; Dyk *et al.*, 1985; Efimov & Naberukhin, 1988; Ben-Naim & Marcus, 1994; Chan & Dill, 1994; Heirata, 2003). Solvent properties are being described by polarity- or experimental multi-parameter systems. While these systems were developed to define the solvent properties only, they are often 'misused' to infer the dissolving properties. To characterise processes of dissolution (process of mixing m), on the other hand, often models are being used that account for both enthalpy ΔH_m and entropy ΔS_m (Nakajima & Huang, 1986; Elbro *et al.*, 1990; Bürgi, 1997), based on the principle of the Flory-Huggins solution theory (Flory, 1942; Huggins, 1942). Looking at the thermodynamic process of dissolving in energetic terms, the following equation must be taken into account (Reichardt, 1990):

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

The requirement for a spontaneous dissolving process is that the Gibbs free energy ΔG_m [J mol^{-1}] of the solution is lowered relative to the undissolved state. This equation describes the energetic situation of a dissolving process, however, without information on the rate of reaction. The enthalpy of mixing ΔH_m, [J mol^{-1}], which corresponds to the commonly known rule of 'like dissolves like', requires similar intermolecular solvent–solvent and solvent–solute forces for successful action. The entropy, in principle, describes the total energy of the system, but since the change of the internal energy (static electric energy, and the different values of the kinetic energy) is negligible during the dissolving process, entropy in this case essentially reflects the strength of the intermolecular interactions. It is mostly positive and in most cases small for dissolving solvents (Reichardt, 1990). Under the ideal situation of maximal chemical affinity

(absolute equivalence of the strength of intermolecular interactions) the resulting entropy value ΔS_m [J K^{-1} mol^{-1}] equals at best 0. In this situation, the system is in equilibrium and no dissolving takes place. The dissolving properties of a material can therefore not be characterised using solvent parametrization systems such as the Teas chart and others. While these models illustrate the theoretical interaction properties of the solvents, they are not capable of describing a dissolving process. Based on the fundamental principle of this thermodynamic rule, 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 (of solvent and solid) and describes the distribution of the solid molecules into the surrounding liquid. This has also been shown to be directly relevant to describe the action of binary solvent mixtures (Zumbühl *et al.*, 2013). The change in entropy is largely dependent on the strength of the intermolecular interactions within the liquid, because the liquid cohesion δ_H^2 has to be overcome first to form a cavity in the liquid prior to incorporating the solute (Chipperfield, 1999). In conclusion, the dissolution comprises endo- and exoenergetic steps. The influence of enthalpy and entropy is schematized in Fig. 1. Since the entropy is strongly influenced by the liquid properties, the solubility of a material, from a theoretical point of view, is ideal when the solute–solvent interactions are good and the solvent cohesion is low. Solubility is not possible if the solvation energy is inadequate. In this case, the enthalpy value ΔH_m is large and cannot be overcompensated by the enthalpy ΔS_m. If the enthalpy value ΔH_m is low, however, a material is also insoluble despite good solvation properties. This case applies to cross-linked solids. The relevance of these two

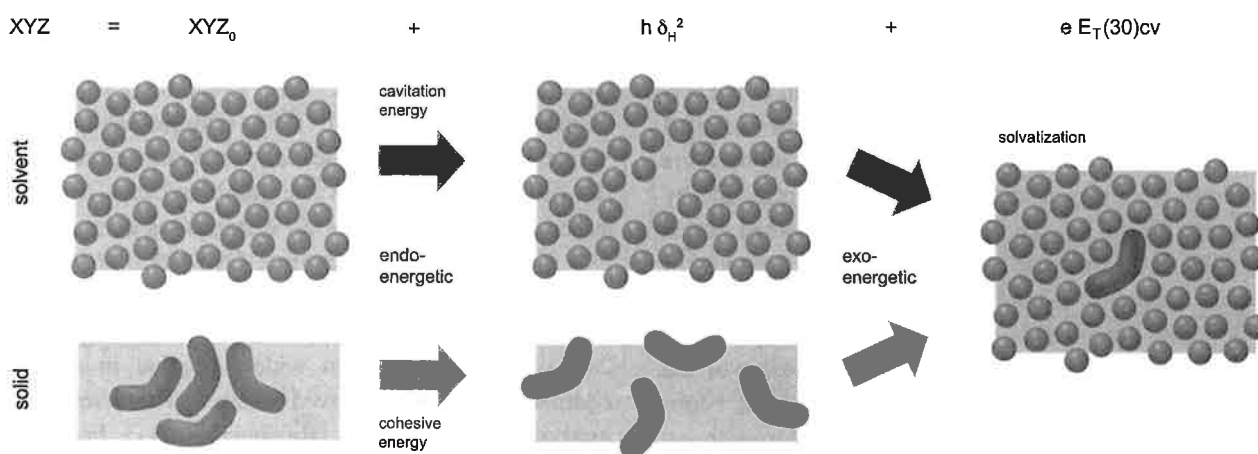**Figure 1** Energetic scheme of the dissolving process after Chipperfield (1999). The endo-energetic cavitation energy $h\delta H^2$ influences the entropy of mixing, while $eE_T(30)cv$ describes the enthalpy of mixing with a specific solute. The $E_T(30)cv$ value is derived from the solvatochromic LSER-values $sSSP + bSB + aSA$ after Catalán (Catalán *et al.*, 1992, 1995, 1996; Catalán & Díaz, 1997).

energetic quantities was investigated for four different paint systems.

Experimental

The maximum swelling capacity of the solvents was quantified (change in volume: $\Delta V/V_0$ max) on four different artists' paint systems representing the solvation capacity of a solute molecule. Experimental tests were applied to commercial tube paints of the following binding media systems: oil (Schmincke® Norma Professional™ (H. Schmincke & Co. GmbH & Co. KG, Ekrath D Winsor & Newton, London GB), product-no. 11704, pigment PBk9, 37 ml), alkyd (Winsor & Newton® Griffin™ (H. Schmincke & Co. GmbH & Co. KG, Ekrath D Winsor & Newton, London GB), product-no. 1302340, pigment PBk9, 37 ml), pure acrylic (Schmincke® PRIMAcryl™ Professional, product-no. 13793, 35 ml, pigment PBk11 and PBk7), and acryl/polystyrene-copolymer (Schmincke® Akademie Acryl™, product-no. 23 771, 60 ml, pigment PBk11 and PBk7) (Zumbühl, 2005; Fuesers & Zumbühl, 2008; Zumbühl *et al.*, 2008). The sample paints were applied to silicone coated PET- foil (Hostaphan® foil RNT 36) using a paint film applicator set to produce a wet film thickness of 300 μm. The oxidative drying paint films were aged over 12 months at 35–40°C applying True Lite® 5500K-daylight and Philips® UV-Light 20W/08 F20 T12 BLB light tubes filtered through a 2 mm window glass. The lighting condition was ≈5800 lm/m² and 557 μW lm⁻¹. The emulsion paint was aged at room conditions for three months (≈55%rF, 19°C). The paint systems were selected based on their chemical nature and not based on conservation needs. Oil and alkyd represent similar hydrocarbon systems, whereas the alkyd (long oily *o*-phthalic acid polyester derivative) is made up of structural elements containing aromatic rings. The same is true for the acrylics and the related styrol copolymer. Furthermore, the evaluated binding systems contain varying amounts of specific chemical groups (e.g. ester groups). This allows the discrimination of the solvation properties in relation to the different chemical nature of the materials. Experiments with 48 solvents (Merck) were run in immersion after the principle by Phenix (2002a, b). The solvents were selected based on chemical aspects to achieve a general overview to a wide range of solvent characteristics. The swelling test was performed on free paint films. The maximum swelling can be used as an indicator of the solvation properties of a system. A segment of 1-mm width was fixed in a circular glass holder with an inner diameter of 4 mm (free length) and designed to inhibit lateral deformation. The swelling power of the solvents was documented with a Wild M5 microscope using sequential imaging. The swelling power

(change in dimension) was quantified by digital image processing applying ImageJ software (version 1.30v, from 'National Institute of Health' NIH, Bethesda (Maryland) USA) (Zumbühl, 2005; Zumbühl *et al.*, 2008).

Parametrization concept of solvent action

The well-founded and empirical 'Linear Solvation Energy Relationship (LSER)' after Kamlet and co-workers (Kamlet *et al.*, 1977, 1981; Kamlet & Taft, 1985) is well established in the field of solvent chemistry (Chapman & Sorter, 1972). This concept parametrises solvents, based on 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 (Taft *et al.*, 1985). This principle forms the theoretical basis for the current work. The new concept applies the purely solvatochromic LSER-system after Catalán (Catalán *et al.*, 1995, 1996; Catalán & Diaz, 1997), which essentially is based on the same theory, but relies on a less complex quantification principle. This additive principle of parametrization to describe the dissolution of a material is expressed as follows:

$$XYZ = XYZ_0 + h\delta_H^2 + sSSP + aSA + bSB \qquad (2)$$

where the parameters of a dissolving process XYZ are the dipolar/polarizability (SSP) value that combines dispersive force interaction, dipole induced interaction and dipole/dipole interaction. The protic (SA) and aprotic (SB) interactions describe the hydrogen bond acceptor and donor properties. XYZ_0 represents the initial state prior to dissolving. Factors h, s, a, and b are solvent-independent coefficients. While the parameters describe the theoretical interaction properties of the solvents, the weighting factors account for their importance relative to the effect on the solute. In addition to these enthalpy values ($sSSP$, aSA, bSB), δ_H^2 describes the cavitation energy of a liquid (equation 2) (Kamlet & Taft, 1985; Symons, 1988; Marcus, 1992; Reichardt, 1994; Chipperfield, 1999). While the system presented above is rather complex, the different interactions are combined in a polarity system, where the sum of all interactions is expressed as a single parameter quantity. Of particular interest in this context is the correlation of these LSER-parameters with the Reichardt $E_T(30)$-value (Reichardt, 2011), a polarity system widely applied in solvent chemistry. Catalán derived these values from the analysis of 138 solvents (Reichardt, 2011). Equation (2) can be simplified using the correlated $E_T(30)$cv values (cv) as follows:

$$XYZ = XYZ_0 + h\delta_H^2 + eE_T(30)cv \qquad (3)$$

In the following, the normalized parameter $[h\delta_H + E_T(30)cv]^N$ will be used as the descriptor of the dissolving properties of a material. Normalized polarity values range from 0 for n-hexane to 100 for water. The calculated polarity value $E_T(30)cv$ describes the magnitude of the enthalpy, and the Hildebrand-Parameter δ_H (cohesive energy of the solvent) accounts for the entropic cavitation energy. According to the extended equation, neither enthalpy nor entropy are independent parameters but are system related, which is accounted for by the factors h and e. In this context, e characterizes the specific interaction situation of solute and solvent, which is defined by the chemical structure of these compounds. The factor h is influenced by the structural segments of the polymers and by the molecular mass of the solid. Their corresponding values were derived experimentally.

Parametrization and classification

The drawback of all polarity systems is the scattering of the individual values from the general trend. This is also true for the new parameter. To account for the large variety of properties of solvents, it makes sense to group the solvents accordingly. This is a strategy often used in the solvent chemistry (Burell, 1955; Liebermann, 1962; Patton, 1964; Chastrette, 1979; Chastrette & Carretto, 1982). By separation of fundamentally different properties, it is possible to improve the specificity of the system. This is visualized in Fig. 2 for the solvent action of non-polar solvents on oil paint. An overall general trend can be read off the swelling graph. Separating the solvents into two individual groups of specific characteristics, two trend curves with low scattering can be fitted. This applies to all four paint systems. In general, it can be stated that the smaller the distance from the trendline, the higher the reliability of the parametrization system to predict the

solvent action. This is essentially what a conservator requires in practice. The selection criteria for such groups comprise both chemical and physical, as well as structural factors. For the classification of the interaction properties, the parameter values by Kamlet and Taft were used: π^* for the dipolarity, α for the protic and β for the aprotic properties. Furthermore, the polarizability polα as well the dipole moment M and the Hildebrand-Parameter δ or δ_H were used (Marcus, 1998). A set of data are listed in Tables 1 and 2. Five groups (I–V) are suggested (Table 2), based on their swelling capacity on four different binding media systems relevant to modern artists' paints. These are summarized in short below:

Group I: Dispersive solvents, such as aliphatic and chlorinated hydrocarbons and esters with π^* values <0.5 and mostly low cavitation energy δ values <19.

Group II: Strongly dispersive and polarisable solvents, such as aliphatic and chlorinated hydrocarbons with π^* values >0.5, as well as strongly polarizable solvents with polα >11.

Group III: Mainly cyclic aprotic solvents combining π^* values >0.5 with β values >0.5.

Group IV: Mainly aliphatic compounds with variable polar groups, as well as cyclic compounds with multiple heteroatoms having π^* values <0.5, additionally strongly dipolar solvents with a dipole moment $M > 3$. Solvents with a large dipole moment could be grouped separately but are classified within group IV to keep the system less complex.

Group V: Strongly protic solvents with α values >0.4. Outliers (non-grouped solvents): Cresols do not fit in any of the above groups. Based on those properties, they must be placed between the protic solvents of groups II and III.

Experimental results

Parametrization within groups thus permits separation of chemically different solvents with similar polarity
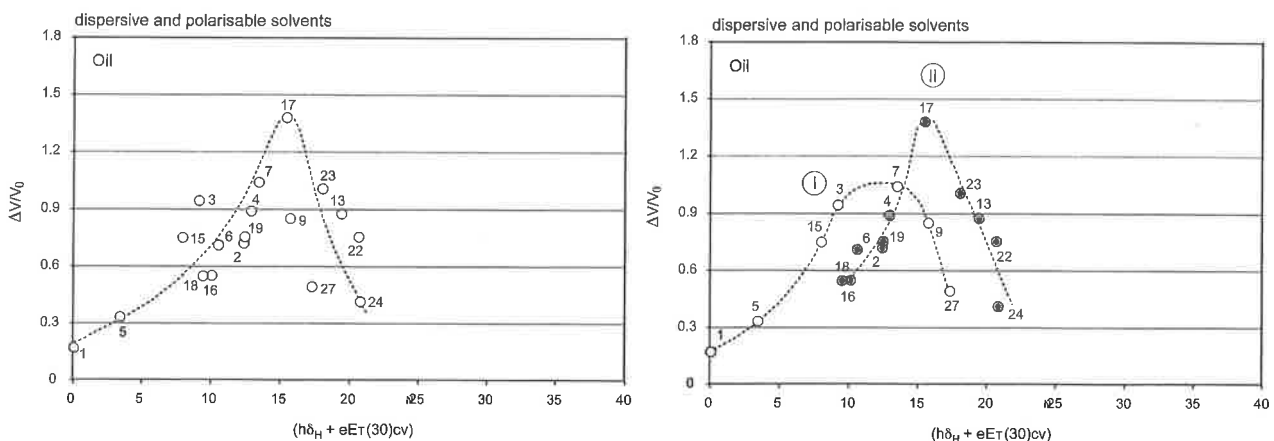
Figure 2 The swelling action of non-polar solvents on oil paint. The *x*-axis represents the new parameter of dissolution, the *y*-axis the swelling capacity. The numbers refer to the solvents in Table 1. The general trend for all solvents exhibits high scattering from any manually fitted trend line (left). Dividing the population into two groups based on specific chemical and physical characteristics (refer to section 'Parametrization and Classification'), a more precise manual fit is achieved. The solvents of group I (white circles) have distinctly smaller cavitation energies than solvents within group II (grey circles).

Table 1 Solvent data

No.	Name	Structural formula	MW	V	d	δ_H	$E_T(30)$	$E_T N$
1	n-Hexane	$CH_3(CH_2)4CH_3$	86.2	131.6	0.6549	15.0	31.0	0.009
2	Tetrachloroethene	$CCl_2 = CCl_2$	165.8	102.7	1.6147	19.0	32.1	0.043
3	Tetrachloromethane	ccu	153.8	97.1	1.5841	17.6	32.4	0.057
4	Toluene	PhMe	92.1	106.9	0.8619	18.8	33.9	0.099
5	Diethyl ether	$C_2H_5OC_2H5$	74.1	104.7	0.7079	15.4	34.5	0.117
6	o-Xylene	$1,2-PhMe_2$	106.1	121.2	0.8760	18.0	34.7	0.123
7	Trichloroethylene	$CCl_2 = CHCl$	131.3	90.0	1.4599	19.0	35.9	0.160
8	1,4-Dioxane	$C-0(CH_2)_2-0-(CH_2)_2-$	88.1	85.7	1.0281	19.7	36.0	0.164
9	1,1,1-Trichloroethane	Cl_3CCHy	133.4	100.3	1.3301	19.6	36.2	0.170
10	Diethyl carbonate	$(C_2H_5O)_2CO$	118.1	121.9	0.9691	17.8	36.7	0.185
11	Tetrahydrofuran	$C-(CH_2)_4-0-$	72.1	81.6	0.8837	19.0	37.4	0.207
12	Butylamine	$CH_3CH_2CH_2CH_2NH_2$	73.1	99.3	0.7366	17.8	37.6	0.213
13	o-Dichlorobenzene	$1,2-PhCl_2$	147.0	113.1	1.2998	20.5	38.0	0.225
14	Ethyl acetate	$CH_3C(0)0C_2H_5$	88.1	98.5	0.8945	18.2	38.1	0.228
15	1,2-Dimethoxyethane	$MeOC_2H_4OMe$	90.1	104.5	0.8624	16.8	38.2	0.231
16	Butyl acetate	$CH_3C(0)0C_4H_9$	116.1	132.5	0.8767	17.6	38.5	0.241
17	Chloroform	$CHCl_3$	119.3	80.7	1.4793	19.5	39.1	0.259
18	Methyl-i-butyl ketone	$MeC(0)CH_2CHMe_2$	100.1	125.7	0.7968	17.2	39.4	0.269
19	1,1-Dichloroethane	Cl_2CHCH_3	99.0	84.7	1.1684	18.3	39.4	0.269
20	Cyclohexanone	$C-(CH_2)_5C(0)-$	98.2	104.2	0.9419	19.7	39.8	0.281
21	Pyridine	$C-(CH)_5N-$	79.1	80.9	0.9778	21.7	40.5	0.302
22	Acetophenone	$PhC(0)Me$	120.1	117.4	1.0234	20.8	40.6	0.306
23	Dichloromethane	CH_2Cl_2	89.9	64.5	1.3943	20.2	40.7	0.309
24	Ethyl formate	$HC(0)0C_2H_5$	74.1	80.9	0.9157	20.9	40.9	0.315
25	Morpholine	$C-0-(CH_2)_2-NH-(CH_2)_2-$	87.1	87.5	0.9957	21.8	41.0	0.318
26	Methyl ethyl ketone	$MeC(0)C_2H_5$	72.1	90.2	0.7884	18.7	41.3	0.327
27	1,2-Dichloroethan	$ClCH_2CH_2Cl$	99.0	79.4	1.2463	20.0	41.3	0.327
28	Acetone	$MeC(0)Me$	58.1	74.0	0.7849	22.1	42.2	0.355
29	N-Methylpyrrolidinone	$C-(CH_2)_3C(0)N(Me)-$	99.1	96.4	1.0283	23.6	42.2	0.355
30	1,3-Dioxolane	$C-0CH_2-0-(CH_2)_2-$	74.1	69.6	1.0644	21.8	43.1	0.383
31	N,N-Dimethylformamide	$HC(0)NMe_2$	73.1	77.4	0.9433	24.1	43.2	0.386
32	t-Butanol	Me_3COH	74.1	94.9	0.7810	21.6	43.3	0.389
33	Propionitrile	CH_3CH_2CN	55.1	70.9	0.7764	21.8	43.6	0.398
34	Acetic anhydride	$CH_3C(0)0C(0)CH_3$	102.0	95.0	1.0746	22.1	43.9	0.407
35	Sulfolane	$C-(CH_2)_4s(0)_2-$	120.1	95.3	1.2610	27.2	44.0	0.410
36	Dimethyl sulfoxide	$MeS(0)Me$	78.1	71.3	1.0958	26.6	45.1	0.444
37	Acetonitrile	CH_3CN	41.1	52.9	0.7760	24.1	45.6	0.460
38	2-Butanol	$C_2H_5CH(OH)CH_3$	74.1	92.3	0.8030	22.6	47.1	0.506
39	2-Propanol	Me_2CHOH	60.1	76.9	0.7815	23.7	48.4	0.546
40	1-Pentanol	C_5HnOH	88.2	108.5	0.8124	22.4	49.1	0.586
41	1-Butanol	C_4H_9OH	74.1	92.0	0.8057	23.3	49.7	0.586
42	1-Propanol	C_3H_7OH	60.1	75.1	0.8003	24.4	50.7	0.617
43	Cellosolve	$C_2H_5OCH_2CH_2OH$	90.1	97.4	0.9253	20.3	51.0	0.627
44	Ethanol	C_2H_5OH	46.1	58.7	0.7848	26.0	51.9	0.654
45	m-Kresole	$3-MePhOH$	108.1	105.0	1.0299	22.1	52.4	0.670
46	p-Kresole	$4-MePhOH$	108.1	106.0	1.0202	22.1	53.3	0.697
47	Glycerol	$HOCH_2CH(OH)CH_2OH$	92.2	73.2	1.2582	33.7	57.0	0.812
48	Methanol	MeOH	32.0	40.7	0.7872	29.3	55.4	0.762
49	Formamide	$HC(0)NH_2$	45.0	39.9	1.1288	39.6	55.8	0.775
50	Water	HOH	18.0	18.1	0.9974	47.9	63.1	1.000

MW, molecular weight [g mol^{-1}]; V, molar volume [cm^3 mol^{-1}]; d, density [g cm^{-3}]; δ, Hildebrand parameter [$J^{1/2}$ $cm^{3/2}$]; $E_T(30)$, Reichardt polarity parameter [kcal mol^{-1}]; E_T^N, normalized Reichardt parameter [-] (Marcus, 1998; Reichardt, 1994, 2011).

Table 2 Solvent data

No.	Name	π^*	α	β	SSP	SA	SB	$E_{T(30)}$ CV	μ	ε	pol α	Group
1	n-Hexane	−0.11	0.00	0.00	0.519	0.000	0.056	31.4	0.1	1.9	11.9	I
2	Tetrachloroethene	0.25	0.00	0.05					0.0	2.3	12.0	II
3	Tetrachloromethane	0.21	0.10	0.00	0.632	0.000	0.440	35.1	0.0	2.2	10.5	I
4	Toluene	0.49	0.00	0.11	0.655	0.000	0.128	34.4	0.3	2.4	12.3	II
5	Diethyl ether	0.24	0.00	0.47	0.694	0.000	0.562	36.8	1.2	4.2	8.9	I
6	o-Xylene	0.51	0.00	0.12	0.641	0.000	0.157	34.2	0.5	2.6	14.2	II
7	Trichloroethylene	0.48	0.00	0.05	0.742		0.069	35.9	0.8	3.4	10.0	I
8	1,4-Dioxane	0.49	0.00	0.37	0.701	0.000	0.444	36.5	0.5	2.2	8.6	IV
9	1,1,1-Trichloroethane	0.44	0.00	0.00	0.850	0.000	0.085	38.1	1.7	7.3	10.4	I
10	Diethyl carbonate	0.40	0.00	0.40					0.9	2.8	11.3	IV
11	Tetrahydroturan	0.55	0.00	0.55	0.838	0.000	0.591	39.8	1.8	7.6	7.9	III
12	Butylamine	0.31	0.05	0.72	0.730	0.000	0.944	39.1	1.4	4.9	9.5	−
13	o-Dichlorobenzene	0.77	0.00	0.03	0.911	0.033	0.144	40.4	2.5	9.9	9.6	II
14	Ethyl acetate	0.45	0.00	0.45	0.795	0.000	0.542	38.8	1.8	6.0	8.8	III
15	1,2-Dimethoxyethane	0.53	0.00	0.41	0.788	0.000	0.636	39.0	1.7	7.2	9.6	I
16	Butyl acetate	0.46	0.00	0.45	0.784	0.000	0.525	38.5	1.8	5.0	12.4	II
17	Chloroform	0.58	0.20	0.10	0.786	0.047	0.071	37.9	1.2	4.9	8.5	II
18	Methyl-l-butyl ketone	0.65	0.02	0.48	0.887	0.000	0.540	40.6	2.7	13.1	11.9	II
19	1,1-Dichloroethane	0.48	0.10	0.10					1.8	10.0	8.4	II
20	Cyclohexanone	0.68	0.00	0.53	0.874	0.000	0.482	40.1	3.1	15.5	11.1	IV
21	Pyridine	0.87	0.00	0.64	0.922	0.033	0.581	42.3	2.4	12.9	9.6	III
22	Acetophenone	0.81	0.04	0.49	0.904	0.044	0.365	41.4	3.0	17.4	7.0	II
23	Dichloromethane	0.82	0.13	0.10	0.876	0.040	0.178	40.0	1.1	8.9	6.5	II
24	Ethyl formate	0.61	0.00	0.36					1.9	7.2	7.0	−
25	Morpholine	0.74	0.29	0.70	0.893	0.000	0.610	41.0	1.6	7.4	9.3	III
26	Methyl ethyl ketone	0.60	0.06	0.48	0.881	0.000	0.520	40.4	2.8	18.1	8.2	IV
27	1,2-Dichloroethan	0.73	0.00	0.10	0.890	0.030	0.126	39.8	1.8	10.4	8.3	I
28	Acetone	0.62	0.08	0.48	0.881	0.000	0.475	40.3	2.7	20.6	6.4	IV
29	N-Methylpyrrolidinone	0.92	0.00	0.77	0.970	0.024	0.613	43.2	4.1	32.2	10.6	III
30	1,3-Dioxolane	0.63	0.00	0.45	0.843	0.000	0.398	39.2	1.5		6.7	IV
31	N,N-Dimethylformamide	0.88	0.00	0.69	0.954	0.031	0.613	43.0	3.8	36.7	7.8	III
32	t-Butanol	0.41	0.42	0.93	0.829	0.145	0.928	44.6	1.7	12.5	8.8	V
33	Propionitrile	0.64	0.00	0.37	0.875	0.030	0.365	40.5	4.0	28.3	6.3	IV
34	Acetic anhydride	0.76	0.00	0.29					2.8	20.6	8.9	IV
35	Sulfolane	0.90	0.00	0.39	1.003	0.052	0.365	43.6	4.8	43.3	10.8	IV
36	Dimethyl sulfoxide	1.00	0.00	0.76	1.000	0.072	0.647	45.1	4.1	46.5	8.0	IV
37	Acetonitrile	0.66	0.19	0.40	0.895	0.044	0.286	40.9	3.9	35.9	4.4	IV
38	2-Butanol	0.40	0.69	0.80	0.842	0.221	0.888	46.6	1.7	16.6	8.8	V
39	2-Propanol	0.48	0.76	0.84	0.848	0.283	0.830	48.0	1.7	19.9	7.0	V
40	1-Pentanol	0.40	0.84	0.86	0.817	0.319	0.860	48.4	1.7	13.9	10.6	V
41	1-Butanol	0.47	0.84	0.84	0.837	0.341	0.809	49.2	1.8	17.5	8.8	V
42	1-Propanol	0.52	0.84	0.90	0.847	0.367	0.782	49.9	3.1	20.5	7.0	V
43	Cellosolve				0.882	0.355	0.560	49.5	2.1	29.6	9.5	V
44	Ethanol	0.54	0.86	0.75	1.000	0.697	0.192	58.9	1.7	24.6	5.1	V
45	m-Kresole	0.68	1.13	0.34					1.5	12.4	13.0	0
46	p-Kresole	0.68	1.64	0.34	0.948	0.653	0.309	57.2	1.5	11.1	13.2	0
47	Glycerol	0.62	1.21	0.51	0.857	0.605	0.545	55.1	4.2	42.5	8.1	V
48	Methanol	0.60	0.98	0.66	0.833	0.549	0.414	52.7	2.9	32.7	3.3	V
49	Formamide	0.97	0.71	0.48	0.962	1.062	0.025	66.6	3.4	109.5	4.2	V
50	Water	1.09	1.17	0.47	0.853	0.400	0.658	50.4	1.9	78.4	1.5	V

π^* [-] α [-] β [-], Kamlet/Taft LSER parameter (Kamlet *et al.*, 1977, 1981a, b; Kamlet & Taft, 1985; Marcus, 1998); SSP [-] SA [-] SB [-], Catalán LSER parameter (Catalán *et al.*, 1992, 1996, Catalán & Diaz, 1997; Wypach, 2001); $E_T(30)$cv, correlated $E_T(30)$ parameter from SSP, SA, SB [$J^{1/2}$ cm$^{3/2}$]; μ, dipole moment [D] (1D = 3.33564 × 10−30 C·m) (Marcus, 1998); ε, Di-electricity constant [-] (Marcus, 1998); αpol, polarizability [10–30 m^3] (Marcus, 1998); solvent groups: I–V
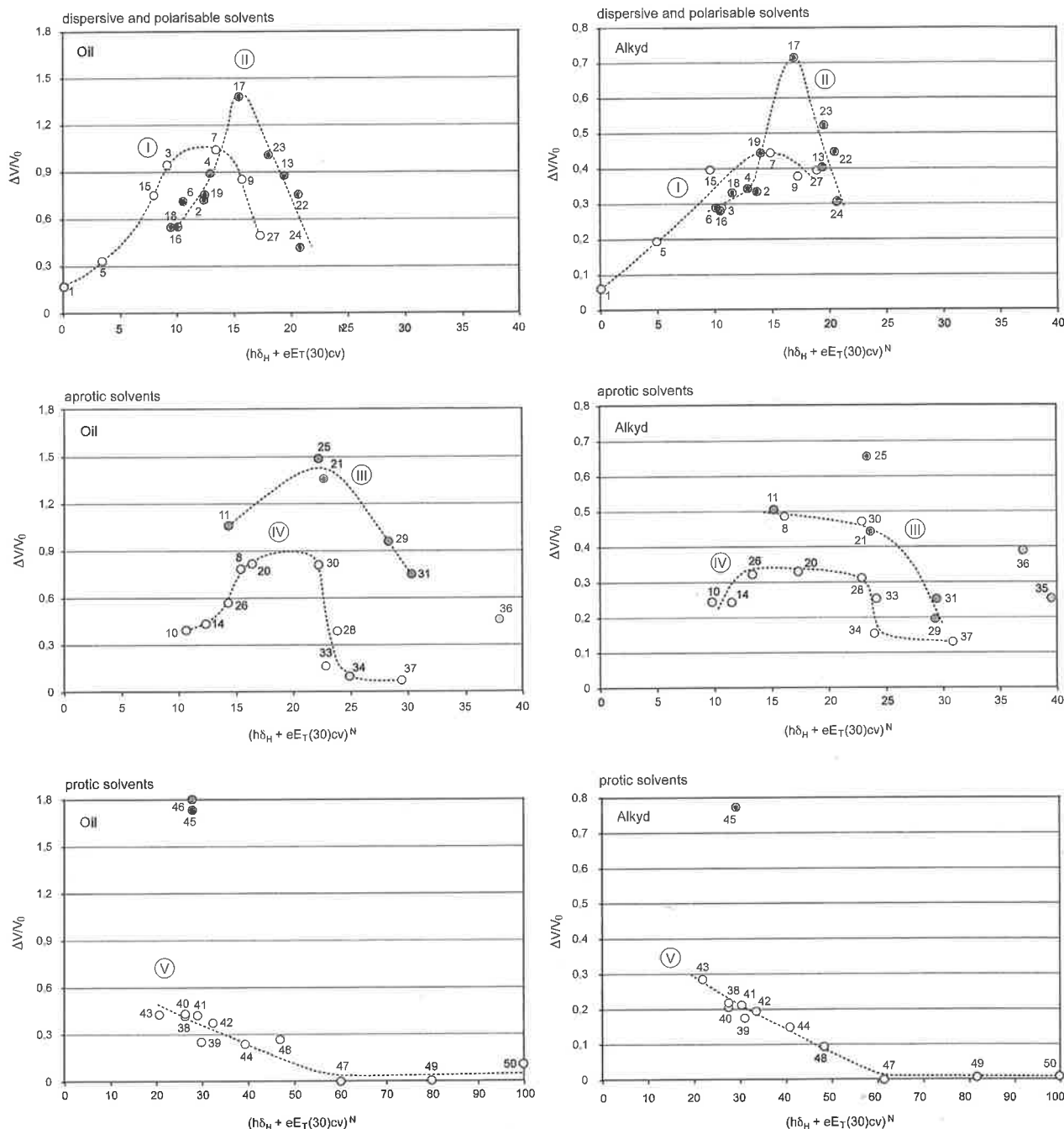
Figure 3 Swelling trends of the individual solvent groups (I–V) for oil paints (left) and alkyd paints (right). The white and grey circles delimit solvents of separate groups classified by their characteristics along a manually fitted trend line.

values. The dissolving potential of each solvent group can thus be represented along an individual polarity axis $[h\delta_H + eE_T(30)cv]^N$ (see equation 3). An overview across the groups could be given using a diagram with multiple polarity axes, adding a second dimension to the system (Patton, 1964). This enables depiction of spatial interaction capacities, while accounting for repulsive and steric hindrance. Since the parameter $[h\delta_H + eE_T(30)cv]^N$ is solute dependent, factors h and e had to be determined experimentally. The best trend with the least scattering was defined for each binding media system, whereby the line is the best graphical fit but not a mathematical function. The following values were derived:

- Oil: $[\delta_H + 0.095\ E_T(30)cv]$
- Alkyd: $[\delta_H + 0.1\ E_T(30)cv]$
- Acrylic-copolymer $[\delta_H + 0.05\ E_T(30)cv]$
- Acrylic/polystyrene-copolymer $[\delta_H + 0.09\ E_T(30)cv]$

The resulting trend curves of all axes (solvent groups) for each of the four binder systems are presented in Figs. 3 and 4. The five individual trend curves were then merged into two-dimensional contour plots of efficiency. For better readability, axes I–III were offset to simplify the presentation of spaces of efficiency. Unlike the ternary teas chart (Teas, 1968; Zumbühl, 2005), graphical offsets do not affect the essence of the system since both absolute
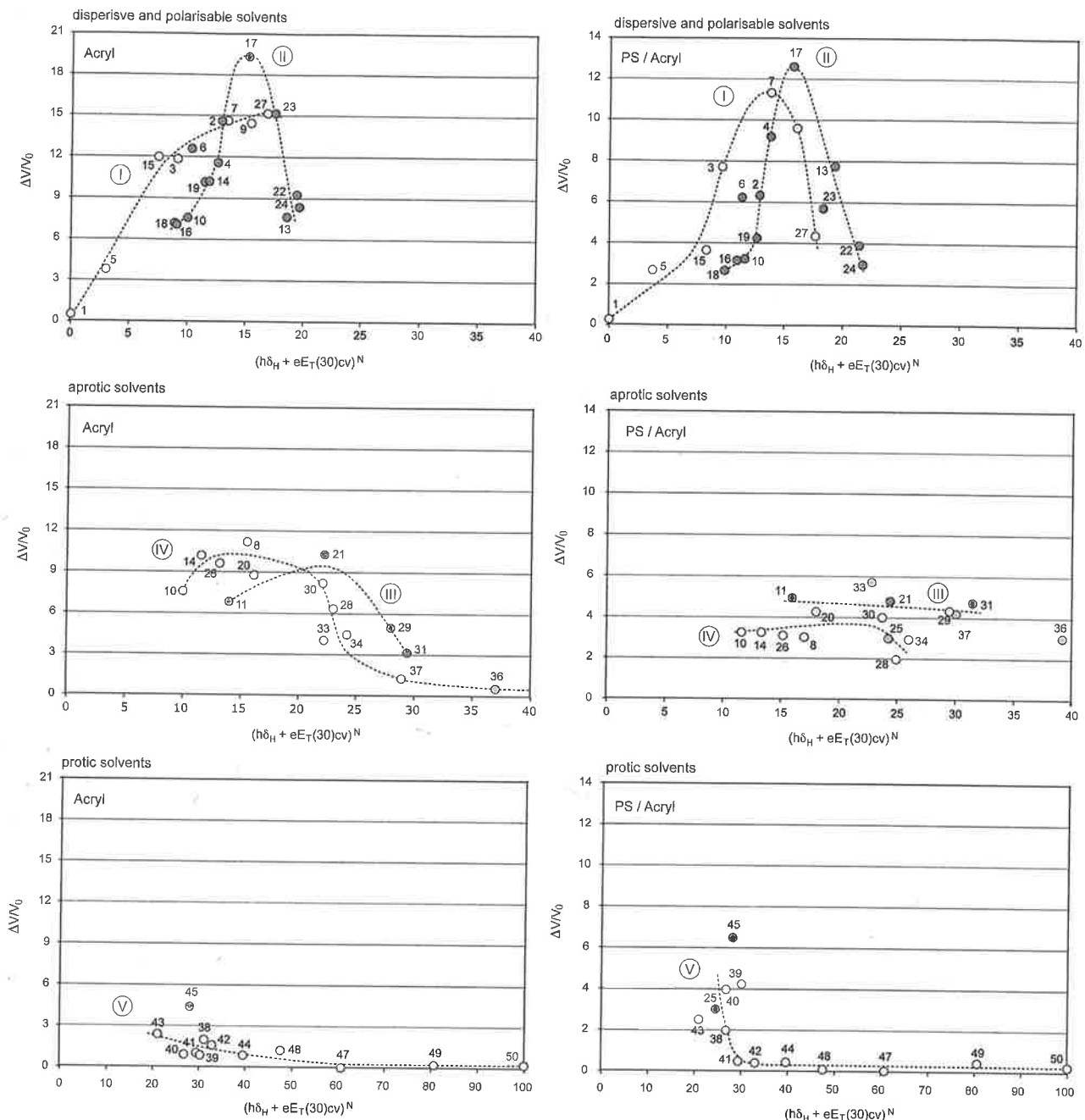
Figure 4 Swelling trends of the individual solvent groups (I–V) for acryl copolymer emulsion paint (left) and acryl/styrene copolymer emulsion paint (right). The white and grey circles again delimit solvents of separate groups classified by their characteristics along a manually fitted trend line.

Discussion

values and scaling remain intact. The swelling capacity of the solvents is displayed as variably sized circles, whereby the diameter corresponds to the relative intensity of action of the different solvents. Absolute values can be read off Figs. 3 and 4 where the grey colour corresponds to the interval along y in Figs. 5 and 6.

Discussion

Overall it can be said that this new parametrization system delivers a very clear graphical distinction while accounting for an enormous variability of solvent properties. The contour plots provide an overview over the general susceptibility of a material to solvent attack. The extent of the corresponding

spaces of efficiency varies considerably and characteristically for each of the four paint systems (Figs. 5 and 6). The charts thus deliver information on the spectrum of solvent susceptibility of these material systems as well as on the selective efficiency of particular solvents. The efficiency maxima are all within group I and II. In general, the unspecific dispersive force interaction with the hydrocarbon backbone of the binder molecules is of higher relevance than the specific interactions with the different functional groups. For this reason, the π^* value is of decisive relevance when defining solvent groups. Furthermore, the results suggest the limitation of dipole–dipole interactions through repulsive effects. The importance
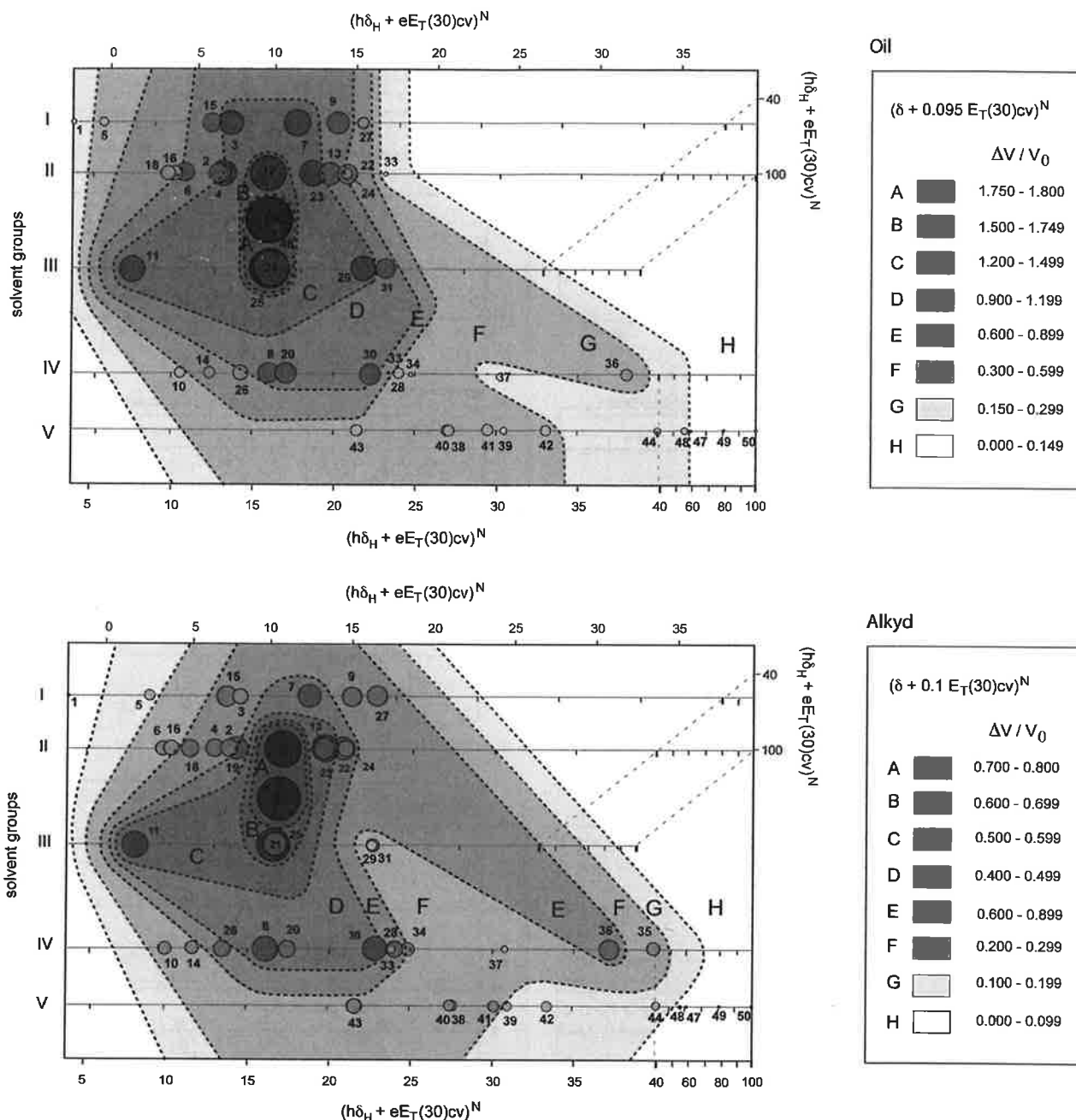
Figure 5 Contour plot of efficiency representing the swelling action of solvents on oil paint (upper) and long-chain alkyd paint (lower). The relative swelling capacity of the solvents is displayed as variably sized circles, whereby the diameter corresponds to the relative intensity of action of the different solvents. The absolute swelling levels (relative change in volume $\Delta V / V_0$) are reproduced in levels of grey (refer to legend). The grey levels correspond to the intervals along y presented in Fig. 3.

of this interaction for the solvatization of a broad range of solutes is thus barely relevant. This observation clearly contradicts with the parametrization developed by Hansen (1995, 2000, 2007) and Teas (1968). Probably, the most relevant point to discuss here is the fact that an increased intermolecular interaction between the solvent and the material does not inevitably lead to a better solubility. This is particularly true for dispersive force interacting solvents. Generally, the increased capacity of interaction is accompanied by an increase of the cohesive energy of the liquid. An increase in the enthalpy value thus leads to a higher cavitation energy of the solvent,

and therefore reduces the entropy. This becomes evident when looking at the swelling trends where the swelling maximum of the solvents of group I and II are shifted and exhibit distinct spectral maxima. The solubility is best when the interaction with the solute is high, while the interaction within the solvent is weak. Data on swelling, however, document that a material can still sufficiently go into solution with poor interaction between solvent and solute, if the cavitation energy of the solvent is low. This is applies to many solvents of group I. The success of the parametrization is thus largely enhanced if the solvents are subdivided into groups of similar characteristics.
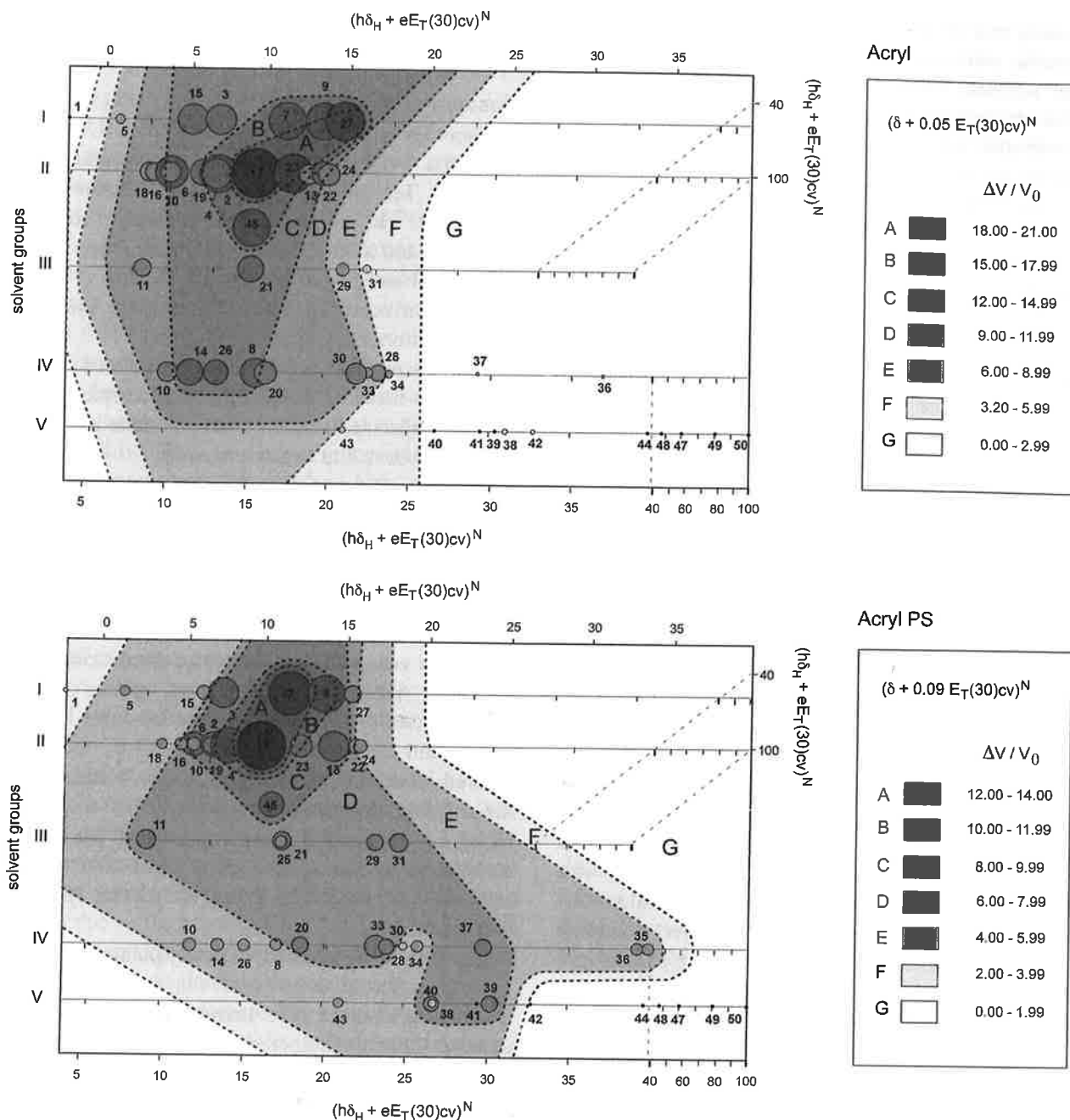
Figure 6   Contour plot of efficiency representing the swelling action of solvents on acrylics (upper) and polystyrene acrylic paint (lower). The relative swelling capacity of the solvents is displayed as variably sized circles, whereby the diameter corresponds to the relative intensity of action of the different solvents. The absolute swelling levels (relative change in volume $\Delta V/V_0$) are reproduced in levels of grey (refer to legend). The grey levels correspond to the intervals along y presented in Fig. 4.

Furthermore, the parametrization unravels the fact that the cavitation energy δ_H has a dominant role in the dissolution of all tested paint systems. This can be derived from the calculated parameter values. It correlates with the theory on non-polar solutes and corresponds to observations made by Kamlet and co-workers, who documented that solubility of these materials are better represented by δ_H than by π^* (Kamlet *et al.*, 1981b). This endo-energetic δ_H is to be regarded as the activation barrier of the dissolution. The balance of the solvation forces described by $eE_T(30)cv$ and the cohesive forces of the solvent parametrized by δ_H thus decisively controls the

dissolving of a binder within a solvent. The solubility of a material therefore does not primarily depend on the intermolecular interaction. It is essential to include the physical solvent properties. The lower the molecular mass of the solute molecule, the more dominant is this effect (Engel, 2011). This finding sets the demand for new concepts with respect to the application of solvents in conservation/restoration treatments. The presented parametrization system is one suggestion on how to incorporate these fundamental aspects. The chosen parametrization criteria successfully differentiate the solvent action on non-polar binder systems such as oils (Fig. 5). This is also

mostly true in the case of alkyd systems, despite the specific solvatization conditions. Parametrization of the acrylics, however, has shown some difficulties, whereby scattering is somewhat higher for the highly polarisable solvents of group II (Fig. 6). This observation can be explained by the variability of repulsive effects of the aprotic groups. While the system has considerable implications and potential, its application in conservation/restoration practice requires more data on the solvent action on a broad range of binding media in order to be validated. Furthermore, it is necessary include the rate of solvent action and entropy change in future studies with particular emphasis on the search for the most decisive factors relevant to the cleaning of artwork with solvents.

Conclusion

Solvent parametrization systems are of considerable interest to problem based and applied working strategies in painted artwork conservation. They are expected to deliver a systematic evaluation of the solvents with a high rate of success and judge the responsibility of action. Since the solvent action is highly influenced by the entropy relevant cavitation energy of the solvent, this finding sets the demand for new concepts in solvent parametrization. The proposed system is based on a combination of different concepts used in solvent chemistry. The parametrization principle builds on the fundamental concept of the LSER. The results indicate that the dissolving of a material cannot exclusively be described by intermolecular interactions. The new parameter combines several relevant factors of the dissolving process into one: it considers the solvent properties, the material-related solvent/solute interaction properties, as well as a system-related entropy value. In summary, the presented parametrization system demonstrates a highly efficient graphical selectivity to describe the solvent efficiency, despite the enormous range of behavioural properties of the solvents. The contour plots quantifying the solvent action on four modern artists' paint systems demonstrate the systematic description of the solvent action of the tested materials. It was possible to derive cohesive spaces of efficiency of distinct levels of action. It is a first step towards the development of a systematic tool aimed at the responsible and reliable use of solvents in the field of conservation/restoration.

Acknowledgements

Glossary

Terminology after IUPAC (International Union of Pure and Applied Chemistry), Compendium of Chemical Terminology Gold Book, version 2.3.2 2012-08-19, <http://goldbook.iupac.org/>, accessed 6.11.2012, and after literature (Zumbühl *et al.*, 2013).

Aprotic (solvent) or non-protogenic: Capable of acting as a proton acceptor. These solvents are hydrogen bond acceptors.

Bond dipole moment: It uses the idea of electric dipole moment to measure the polarity of a chemical bond within a molecule. It occurs whenever there is a separation of positive and negative charges.

Catalán solvent parameters: LSER-parameters of this solvatochromic relationship which measure separately the hydrogen bond donor (SA), hydrogen bond acceptor (SB), and dipolarity/polarisability (SSP) properties of solvents as contributing to overall solvent polarity.

Cavitation energy: Is the energy of formation of the hole that preserves the dissolved species in the solvent (see: cohesive energy of the liquid, Hildebrand parameter).

Dimroth–Reichardt parameter $E_T(30)$: A measure of the ionizing power (loosely polarity) of a solvent, based on the maximum wavenumber of the longest wavelength electronic absorption band of a specific solvatochromic indicator in a given solvent (polarity parameter).

Dipole–dipole interaction: Intermolecular interaction between molecules or groups having a permanent electric dipole moment. The strength of the interaction depends on the distance and relative orientation of the dipoles.

Dipole-induced dipole forces: Intermolecular interaction between dipolar molecules with polarisable groups of a neighbouring molecule.

Dissolution: Dissolution is a kinetic process, and is quantified by its rate. Refers to the mixing of two phases with the formation of one new homogeneous phase (solution).

Enthalpy H: Is a measure of the total energy of a thermodynamic system. It includes the internal energy, which is the energy required to create a system, and the amount of energy required to make room for it by displacing its environment and establishing its volume and pressure.

Entropy S: Is a thermodynamic property that is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.

Hildebrand parameter δ_H: A parameter measuring the cohesion of a solvent (energy required to create a cavity in the solvent: Cavitation energy).

Hydrogen bond: A form of association between an electronegative atom (aprotic group) and a hydrogen atom (protic group) attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges.

Kamlet–Taft solvent parameters: LSER Parameters of the Kamlet–Taft solvatochromic relationship which measure separately the hydrogen bond donor (α), hydrogen bond acceptor (β), and dipolarity/polarizability (π^*) properties of solvents as contributing to overall solvent polarity.

London forces (synonym: dispersion forces): Attractive forces between apolar molecules, due to their mutual polarizability. They are also components of the forces between polar molecules. Also called 'dispersion forces'.

LSER: Linear solvation energy relationships: Equations involving the application of solvent parameters in linear or multiple (linear) regression expressing the solvent effect on the rate or equilibrium constant of a reaction.

Polarity: When applied to solvents, this rather ill-defined term covers their overall solvation capability (solvation power) for solutes, which in turn depends on the action of all possible, nonspecific and specific, intermolecular interactions between solute and solvent molecules.

Polarizability: The ease of distortion of the electron cloud of a molecular entity by an electric field (such as that due to the proximity of a charged reagent). It is experimentally measured as the ratio of induced dipole moment to the field that induces it.

Polymer–solvent interaction: The sum of the effects of all intermolecular interactions between polymer and solvent molecules in solution that are reflected in the Gibbs and Helmholtz energies of mixing.

Protic or protogenic (solvent): Capable of acting as a proton donor (strongly or weakly acidic as a Brønsted acid). These solvents are hydrogen bond donors.

Solubility: Solubility quantifies the dynamic equilibrium. The proportion of a designated solute in a designated solvent, is the solubility of that solute. The solubility may be expressed as a concentration, molality, mole fraction, mole ratio, etc.

Solute: The minor component of a solution (as example a polymer molecule), which is regarded as having been dissolved by the solvent.

Solution (also contains definition of solvent): A liquid or solid phase containing more than one substance, when for convenience one (or more) substance, which is called the solvent, is treated differently from the other substances, which are called solutes.

Solvation: The solvation is the process of attraction and association of molecules of a solvent with molecules. It describes the interaction of a solute and the solvent or a similar interaction of solvent with groups of an insoluble material. Such interactions generally involve electrostatic forces and van der Waals forces, as well as chemically more specific effects such as hydrogen bond formation.

Solvation energy: The change in Gibbs energy when molecule is transferred from a vacuum (or the gas phase) to a solvent. The main contributions to the solvation energy come from: the cavitation energy of formation of the hole (cavity), which preserves the dissolved species within the solvent, the orientation energy and the interaction energy.

Solvatochromism: The (pronounced) change in position and sometimes intensity of an electronic absorption or emission band, accompanying a change in the polarity of the medium.

Solvent parameters: Quantitative measures of the capability of solvents for interaction with solutes. Such parameters have been based on numerous different physicochemical quantities, solvatochromic shifts (solvatochromism) in ultraviolet/visible spectra etc. Some solvent parameters are purely empirical in nature, i.e. they are based directly on some experimental measurement. It may be possible to interpret such a parameter as measuring some particular aspect of solvent–solute interaction or it may be regarded simply as a measure of solvent polarity.

Steric hindrance: The original term for a steric effect arising from crowding of substituents. The intermolecular interactions are limited by the availability of the functional groups based on the arrangements of atoms of a molecular entity in space.

Van der Waals forces: The attractive or repulsive forces between molecular entities other than those due to bond formation or to the electrostatic interaction. The term includes: dipole–dipole, dipole-induced dipole and London (instantaneous induced dipole-induced dipole) forces. The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces.

References

Banik, G. & Krist, G. 1984. *Lösungsmittel in der Restaurierung.* Wien: Verlag der Apfel.

Barton, A.F.M. 1991. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters.* Boca Raton: CRC Press.

Ben-Naim, A. & Marcus, Y. 1994. Solvation Thermodynamics of Nonionic Solutes. *Journal of Chemical Physics,* 81: 2016–27.

Burell, H. 1955. Solubility Parameters for Film Formers. *Official Disgest, Federation of Societies for Paint Technology,* 27: 726–58.

Bürgi, R. 1997. *Computer Simulations on the Flory-Huggins Theory in Polymer Physics.* Diplomarbeit: Universität Bern.

Catalán, J. & Diaz, J. 1997. A Generalized Solvent Acidity Scale – The Solvatochromism of o-tert-Butylstilbazolium Betaine Dye and its Homomorph o-o'-Di-tert-butylstilbazolium Betaine Dye. *Liebigs Annalen der Chemie,* 1997: 1941–9.

Catalán, J., Mena, E., Meutermans, W. & Elguero, J. 1992. Solvatochromism of a Typical Merocyanine – Stilbazplium

Betaine and its 2,6-di-tert-Butyl Derivative. *Journal of Physical Chemistry*, 96: 3615–21.

Catalán, J., Lopez, V., Perez, P., Martin-Villamil, R. & Rodriguez, J.-G. 1995. Progress Toward a Generalized Solvent Polarity Scale – The Solvatochromism of 2-(Dimethylamino)-7-nitro-fluorene and its Homomorph 2-Fluoro-7-Nitrofluorene. *Liebigs Annalen der Chemie*, 1995: 241–51.

Catalán, J., Diaz, C., Lopez, V., Perez, P., Paz, J.-L.D. & Rodriguez, J.G. 1996. A Generalized Solvent Basicity Scale – The Solvatochromism of 5-Nitroindoline and its Homomorph 1-Methyl-5-nitroindoline. *Liebigs Annalen der Chemie*, 1996: 1785–94.

Chan, H.S. & Dill, K.A. 1994. Solvation – Effects of Molecular Size and Shape. *The Journal of Chemical Physics*, 101: 7007–26.

Chapman, N.B. & Sorter, J. eds. 1972. *Advances in Linear Fee Energy Relationship*. London: Plenum Press.

Chastrette, M. 1979. Statistical Study of Solvent Effects – I. Principles and Applications to the Evaluation of Solvent Parameters and to Classification. *Tetrahedron*, 35: 1141–8.

Chastrette, M. & Carretto, J. 1982. Statistical Study of Solvent Effects – II. Analysis of Some Empirical Parmeters of Solvent Polarity. *Tetrahedron*, 38: 1615–8.

Chipperfield, J.R. 1999. *Non-aqueous Solvents*. Oxford: Oxford University Press.

Christenson, H.K. & Horn, R.G. 1985. Solvation Forces Measured in Non-Aqueous Liquids. *Chemica Scripta*, 25: 27–41.

Dyk, J.W.V., Frisch, H.L. & Wu, D.T. 1985. Solubility, Solvency and Solubility Parameters. *Industrial and Engineering Chemistry – Product Research and Development*, 24: 473–8.

Efimov, Y.Y. & Naberukhin, Y.I. 1988. Fluctuation Theory of Hydrogen Bonding in Liquids. In: M.C.R. Symons, ed. *Solvation, Faraday Discussions of the Chemical Society*. London: The Royal Society of Chemistry, pp. 117–23.

Elbro, H.S., Fredenslund, A. & Rasmussen, P. 1990. A New Simple Equation for the Prediction of Solvent Activities in Polymer Solutions. *Macromolecules*, 23: 4707–14.

Engel, N. 2011. Evaluation of Retouching Media for Acrylic Emulsion Paint – Aesthetic Integration, Reversibility and Morphological Changes. Master Thesis, Conservation & Restoration, Bern University of Applied Sciences.

Flory, P.J. 1942. Thermodynamics of High Polymer Solutions. *Journal of Chemical Physics*, 10: 51–61.

Fuesers, O. & Zumbühl, S. 2008. The Influence of Organic Solvents to the Mechanical Properties of Alkyd and Oil Paints. In: Art2008: Proceedings of the 9th International Conference on NDT of Art, Jerusalem May 25–30, 2008 [accessed 25 May 2013]. Available at: <http://www.ndt.net/article/art2008/papers/219Fuesers.pdf>

Gardon, J.L. & Teas, J.P. 1976. Solubility Parameters. In: R.R. Myers & J.S. Long, eds. *Treatise on Coatings*. New York: Marcel Dekker.

Gutmann, V. 1977. *The Donor–Acceptor Approach to Molecular Interaction*. New York: Plenum Press.

Hansen, C.M. 1995. Solubility Parameters. In: J.V. Kolkese, ed. *Paint Testing Manual 17*. Philadelphia: American Society for Testing and Materials, pp. 383–404.

Hansen, C.M. 2000. *Hansen Solubility Parameters – A User's Handbook*. Boca Raton: CRC Press.

Hansen, C.M. 2007. *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*. Boca Raton: CRC Press, Taylor & Francis Group.

Heirata, F. 2003. *Molecular Theory of Solvation*. New York: Kluwer Academic Publishers.

Hoy, K.L. 1975. *Tables of Solubility Parameters*. Tarrytown, NY: Union Carbide Corporation.

Huggins, M.L. 1942. Thermodynamic Properties of Solutions of Long-Chain Compounds. *Annals of the New York Academy of Science*, 18: 1–32.

Kamlet, M.J. & Taft, R.W. 1985. Linear Solvation Energy Relationships. Local Empirical Roles – or Fundamental Laws of Chemistry? A Reply to the Chemometricians. *Acta Chemica Scandinavica*, B39: 611–28.

Kamlet, M.J., Abboud, J.-L.M., Abraham, M.H. & Taft, R.W. 1977. Linear Solvation Energy Relationships – A Comprehensive Collection of the Solvatochromic Parameters, π*, α, and β, and some Methods for Simplifying the Generalized Solvatochromic Equations. *Journal of Organic Chemistry*, 48: 2877–87.

Kamlet, M.J., Abboud, J.-L.M. & Taft, R.W. 1981a. An Examination of Linear Solvation Energy Relationship. In:

R.W. Taft, ed. *Progress in Physical Organic Chemistry*. New York: John Wiley & Sons, pp. 2877–87.

Kamlet, M.J., Carr, P.W., Taft, R.W. & Abraham, H. 1981b. Linear Solvation Energy Relationships – 13. Relationship between the Hildebrand Parameter δH, and the Solvatochromic Parameter, π*. *Journal of the American Chemical Society*, 103: 6062–6.

Liebermann, E.P. 1962. Quantification of the Hydrogen Bonding Parameter. *Official Disgest, Federation of Societies for Paint Technology*, 34: 30–50.

Lorentz, G. 1998. *Mit Lösemitteln rechnen*. Hamburg: Eigenverlag.

Marcus, Y. 1992. The Structuredness of Solvents. *Journal of Solution Chemistry*, 21: 1217–30.

Marcus, C.M. 1998. *The Properties of Solvents*. Chichester: John Wiles & Sons.

Nakajima, N. & Huang, C.D. 1986. On the Lattice Theory, Free Volume Theory, and Effective Volume Theory of Thermodynamis of Polymer Solutions. *Journal of Macromolecular Science – Part B*, 25: 395–404.

Nigam, S. & Rutan, S. 2001. Principles and Applications of Solvatochromism. *Applied Spectroscopy*, 55: 362A–70A.

Oakey, N.L. & Morokuma, K. 1975. A Simple Model of Solvation within the Molecular Orbital Theory. *Chemical Physical Letters*, 36: 465–9.

Patton, C. 1964. Solubility and Solvent Volatility, Chapter 13. In: C. Patton, ed. *Paint Flow and Pigment Dispersion – A Rheological Approach to Coating and Ink Technology*. New York: Interscience Publishers, pp. 349–85.

Phenix, A. 1998. Solubility Parameters and the Cleaning of Paintings – An Update and Review. *Zeitschrift für Kunsttechnologie und Konservierung*, 12: 387–409.

Phenix, A. 2002a. The Swelling of Artists' Paints by Organic Solvents and the Cleaning of Paintings – Recent Perspectives, Future Directions. In: H.M. Parkin, ed. *Postprints of the Paintings Specially Group Meeting*. American Institute for Conservation, pp. 71–86.

Phenix, A. 2002b. The Swelling of Artists' Paints in Organic Solvents – Part 2: Comparative Swelling Powers of Selected Organic Solvents and Solvent Mixtures. *Journal of the American Institute for Conservation*, 41: 61–90.

Phenix, A. 2013, Effects of Organic Solvents on Artists' Oil Paint Films: Swelling. In: M.F. Mecklenburg, E.A. Charola & R.J. Koestler, eds. *New Insights into the Cleaning of Paintings: Proceedings of the Cleaning 2010 International Conference Politécnica de Valencia and Museum Conservation Institute*. Washington, DC: Smithsonian Institution Scholarly Press, Smithsonian Contributions to Museum Conservation 3, pp. 69–76.

Pietsch, A. 2002. *Lösemittel – Ein Leitfaden für die restauratorische Praxis*. Stuttgart: Theiss Verlag.

Reichardt, C. 1990. *Solvents and Solvent Effects in Organic Chemistry*. Weinheim: VCH Verlagsgesellschaft.

Reichardt, C. 1994. Solvatochromic Dyes as Solvent Polarity Indicators. *Chemical Reviews*, 94: 2319–58.

Reichardt, C. 2011. *Solvents and Solvent Effects in Organic Chemistry*. Weinheim: Wiley-VCH.

Saera Vila, A. & Barros Garcia, J.M. 2013. Computer Applications and Cleaning – Teas Fractional Solubility Parameter System in Conservation. In: M.F. Mecklenburg, E.A. Charola & R.J. Koestler, eds. *New Insights into the Cleaning of Paintings: Proceedings of the Cleaning 2010 International Conference Politécnica de Valencia and Museum Conservation Institute*. Washington, DC: Smithsonian Institution Scholarly Press, Smithsonian Contributions to Museum Conservation 3, pp. 35–8.

Symons, M.C.R. 1988. *Solvation*. London: The Royal Society of Chemistry.

Taft, R.W., Abboud, J.-L.M., Kamlet, M.J. & Abrahem, H. 1985. Linear Solvation Energy Relations. *Journal of Solution Chemistry*, 14: 153–68.

Teas, J.P. 1968. Graphic Analysis of Resin Solubility. *Journal of Paint Technology*, 40: 19–25.

Torraca, G. 1978. *Solubility and Solvents for Conservation Proplem*, 2nd ed. Rome: ICCROM (International Centre for the Study of the Preservation and the Restoration of Cultural Property).

Wypach, G. 2001. *Handbook of Solvents*. New York: Chem Tech Publishing, William Andrew Publishing.

Zumbühl, S. 2005. Illusion mit System: Das Lösemitteldreieck in der Praxis – Aspekte zur Charakterisierung der Wirkung von

binären Lösemittelmischungen. *Zeitschrift für Konservierung und Restaurierung*, 19: 253–62.

Zumbühl, S., Francesca, A., Scherrer, N., Müller, W., Fenners, N. & Caseri, W. 2008. Solvent Action on Dispersion Paint Systems and the Influence on the Morphology – Changes and Destruction of the Latex Microstructure. In: T. Learner, ed. *Modern Paint Uncovered*. Los Angeles and London: The Getty Conservation Institute and Tate Modern, pp. 255–66.

Zumbühl, S., Ferreira, E.S.B., Scherrer, N.C. & Schaible, V. 2013. The Non-Ideal Action of Binary Solvent Mixtures on Oil and Alkyd Paint. In: M.F. Mecklenburg, E.A. Charola & R.J. Koestler, eds. *New Insights into the Cleaning of Paintings: Proceedings of the Cleaning 2010 International Conference Politécnica de Valencia and Museum Conservation Institute*. Washington, DC: Smithsonian Institution Scholarly Press, Smithsonian Contributions to Museum Conservation 3, pp. 97–105.