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Invited Review

The Solvent-Like Nature of Silica Particles in Organic Solvents

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Summary. *Kamlet-Taft*'s α (hydrogen bond donor acidity) and π^* (dipolarity/polarizability) values of various silica batches measured in various solvents are presented. The α and π^* parameters for the various solid acids are analyzed by means of Fe(*phen*)$_2$(CN)$_2$ (*cis*-dicyano-*bis*-(1,10)-phenanthroline-iron(II), **1**), *Michler*'s ketone (4,4′-*bis*-(dimethylamino)-benzophenone, **2**), and two hydrophilic derivatives of **2**, (4-(dimethylamino)-4′-(di-2-hydroxyethyl)-amino-benzophenone (**3a**) and 4,4′-*bis*-(di-(2-hydroxyethyl)-amino)-benzophenone (**3b**) as well as coumarin 153 (**4**) as solvatochromic surface polarity indicators. Apparent β (hydrogen bond acceptor basicity) parameters for bare silica have been evaluated by means of an aminobenzodifuranone dye (**5**) as solvatochromic probe.

The chemical interpretation of the α and π^* parameters and the nature of the solvent/surface interaction which they reflect are discussed. It can be shown that an increase of the HBA (hydrogen bond accepting) capacity of the solvent significantly decreases the HBD (hydrogen bond donating) capacity of the surface environment, whereas the dipolarity/polarizability value of the silica/solvent interface is a composite of many effects. The classification of the polarity of silica particles in organic solvents compared to pure liquids is outlined.

Theoretical $E_T(30)$ values of the solid/solvent interfaces are calculated by applying linear solvation energy (LSE) relationships using the independently measured α and π^* values of the solid acids according to $E_T(30) = (E_T(30))_o + a\alpha + s\pi^*$.

Keywords. Donor-acceptor effects; Silica; Solvent effect; Surface polarity; UV/Vis spectroscopy.

Introduction

Solvent polarity is among the most widely used concepts in chemistry [1–9] (see Refs. [2–4], [7], and [9] for reviews). Most solvent polarity scales are empirical and based on kinetic, thermodynamic, or spectroscopic data relating to certain reference reactions [2–9]. Different empirical solvent polarity scales have been shown to correlate well with each other, pointing to the existence of an underlying common feature [3, 7–9]

As a consequence of this established concept in solution chemistry, there have been recent considerations of the changes in surface polarity associated with

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structural variations in organically functionalized silica particles including stationary chromatographic phases, various kinds of bare silica particles, and other solid acids [10–25].

However, the interaction of a surface environment with a solvent or an adsorbed molecule is a composite of many effects [11, 13, 19, 23–25]. Not only acid-base, but also dipole-dipole, induced dipole-dipole, and dispersion forces contribute to the overall adsorption energy of a solvent with an inorganic surface. To date, no general agreement upon a definition of the term surface polarity has emerged [21]. In the broadest and most general sense, the surface polarity can be viewed as the sum of all interactive forces between an adsorbed molecule and the occupied surface site or sites. This definition is based on the related interpretation of the term solvent polarity [1].

Multiple intermolecular solute/solvent interactions can be described by the LSE (linear solvation energy) relationship of *Kamlet* and *Taft* [7, 26] (Eq. 1).

$$XYZ = (XYZ)_o + m\delta_H^2 + a\alpha + b\beta + s(\pi^* + d\delta) \quad (1)$$

$(XYZ)_o$ is the solute property of a reference system, *e.g.* a nonpolar medium, δ_H^2 is a cavity term which relates to the *Hildebrandt* solubility parameter, α describes the HBD (hydrogen bond donating) acidity, β the HBA (hydrogen bond accepting) ability, and π^* the dipolarity/polarizability of the solvents. δ is a polarizability correction term which is 1.0 for aromatic, 0.5 for polyhalogenated, and zero for aliphatic solvents; *m*, *a*, *b*, *s*, and *d* are solvent-independent correlation coefficients [7, 26].

Empirical solvent polarity scales based on spectroscopic measurements usually employ changes in the UV/Vis absorption maximum of an indicator in different solvents (solvatochromism) [2, 6, 7]. Visible probing with suitable indicator dyes has also been recommended by several authors for investigating the surface polarities of solids [10–25].

Among others, *Marcus* has shown that the well established empirical $E_T(30)$ solvent polarity parameter and other polarity scales can be expressed by LSE relationships using the *Kamlet-Taft* solvent parameters α and π^* [2, 3].

Presuming a solvent-like behaviour for a surface environment, it is expected that an adsorbed solvatochromic probe reflects contributions of each of these interactions relating to a certain set of α, β, and π^* values, respectively, of the occupied surface site by shifts of its UV/Vis absorption maximum (ν_{max}). The simplified *Kamlet-Taft* LSE equation applied to single solvatochromic shifts, $XYZ = \nu_{max}(\text{probe})$ [2], is given in Eq. (2). Because volume changes do not contribute to $\nu_{max}(\text{probe})$ during electronic transition, the $m\delta_H^2$ term can be neglected.

$$\nu_{max}(\text{probe}) = (\nu_{max}(\text{probe}))_0 + a\alpha + b\beta + s(\pi^* + d\delta) \quad (2)$$

The position of the UV/Vis absorption maximum of the adsorbed dye ($\nu_{max}(\text{probe})$) has been used as a unit for surface polarity [11, 19]. As a consequence of this relation, the knowledge of two precise LSE equations (Eqs. (3a) and (3b)) for two different probes, where the solvent-independent coefficients *a* and *s* are known, is theoretically required in order to determine the pair α and π^* of an unknown material. Usually, for the determination of the underlying LSE equations, the

solvatochromic probes are measured in more than 20 solvents which serve as the reference system [3, 27–30].

Then, the molecular probes Fe(*phen*)$_2$(CN)$_2$ (*cis*-dicyano-*bis*-(1,10)-phenanthroline-iron(II), **1**) and *Michler*'s ketone (4,4′-*bis*-(dimethylamino)-benzophenone, **2**) can be adsorbed on the solid material (or environment) of interest in order to determine $\nu_{max}(\mathbf{1})$ and $\nu_{max}(\mathbf{2})$, respectively. For example, $(\nu_{max}(\mathbf{1}))_0$ denotes the UV/Vis absorption maximum of probe **1** in a nonpolar reference environment.

$$\nu_{max}(\mathbf{1}) = f_1(\alpha, \pi^*) = (\nu_{max}(\mathbf{1}))_0 + a_1'\alpha + s_1'\pi^* \tag{3a}$$

$$\nu_{max}(\mathbf{2}) = f_2(\alpha, \pi^*) = (\nu_{max}(\mathbf{2}))_0 + a_2''\alpha + s_2''\pi^* \tag{3b}$$

In earlier reports we were able to show that a correlation analysis of the desired polarity parameter with the solvatochromic UV/Vis absorption maxima of two structural different polarity indicators according to Eq. 4 seems better suited for determining polarity parameters than are the functions according to Eqs. (3a) and (3b) [19, 28, 30].

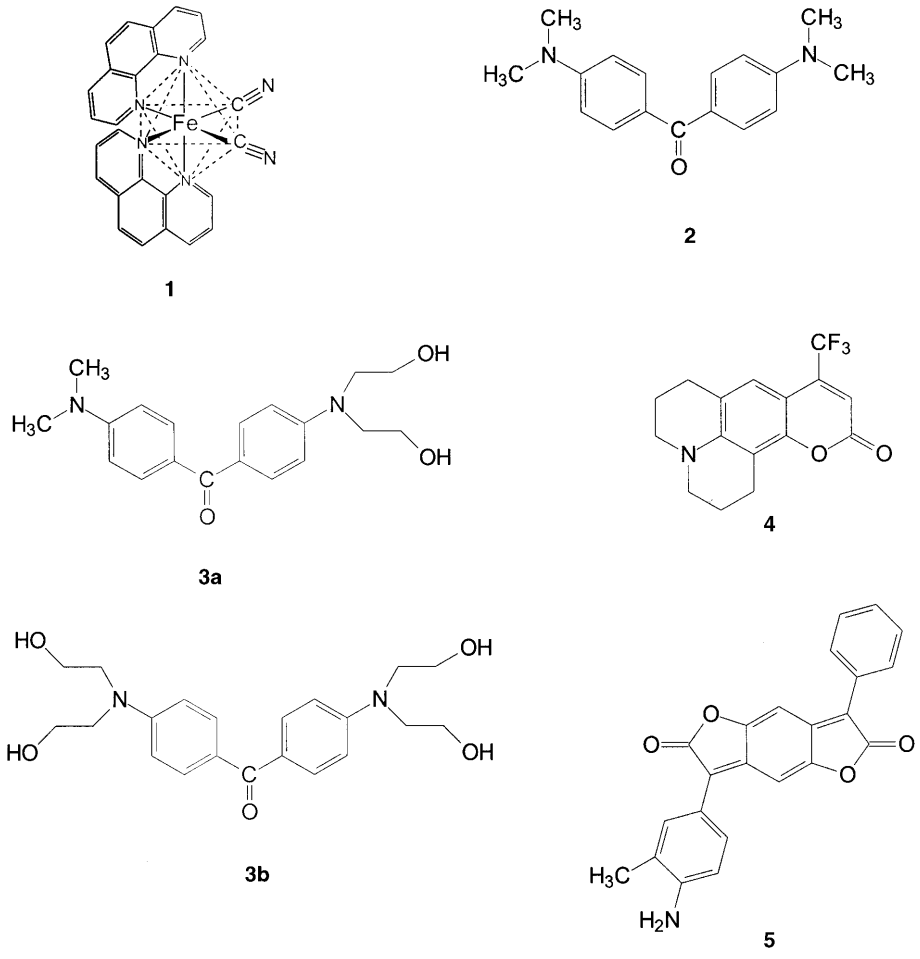
$$\alpha = f(\nu_{max}(\mathbf{1}), \nu_{max}(\mathbf{2})) = a_0 + a_1\nu_{max}(\mathbf{1}) + a_2\nu_{max}(\mathbf{2}) \tag{4}$$

This is true when additional influences of the solvent, *i.e.* derived from the hydrophobicity or size (cavity effect) of the probes, on each ν_{max} are similar [30]. Thus, systematic solvation effects on $\nu_{max}(\mathbf{1})$ and $\nu_{max}(\mathbf{2})$, which are not included in the original α or π^* solvent parameters, then can be better excluded.

It is not easy to decide an adequate probe pair which is suited for an accurate determination of surface polarity parameters of solid materials [19, 30–32]. The following solvatochromic probe molecules have been well established as surface polarity indicators for several applications during the recent years: 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate (*Reichardt*'s standard dye) and various substituted derivatives [10–12, 18, 23], Fe(*phen*)$_2$(CN)$_2$ (**1**) [11, 23, 31, 32], and *Michler*'s ketone (**2**) [11, 23, 31, 32]. Indicator formulas are shown in Scheme 1.

Fe(*phen*)$_2$(CN)$_2$ has been well established as HBD indicator for solvents as well as for solid materials. For instance, its UV/Vis absorption can be used for determining *AN* (acceptor number) of a variety of materials [27]. For separation of the contribution of the α term, we used in particular the ν_{max} values from Fe(*phen*)$_2$(CN)$_2$ and *Michler*'s ketone measured in the same solvents (taken from Refs. [27] and [29]). Multiple square analyses were performed for several dual combinations of $\nu_{max}(\mathbf{1})$ and ν_{max} of other indicators including coumarin 153 (**4**) [30]. However, two solvatochromic probe pairs have been found suitable as α indicators. For determining α values of polysaccharides and silicas, the use of $\nu_{max}(\mathbf{1})$ and $\nu_{max}(\mathbf{2})$ or $\nu_{max}(\mathbf{4})$ has been recommended [19]. A suitable probe pair for the determination of independent π^* parameters for moderately strong solid acids has not yet been established [11, 29, 30]. However, in Ref. [30] we have recommended the probe pair **1** and **4** for determining reasonable π^* parameters of polysaccharides.

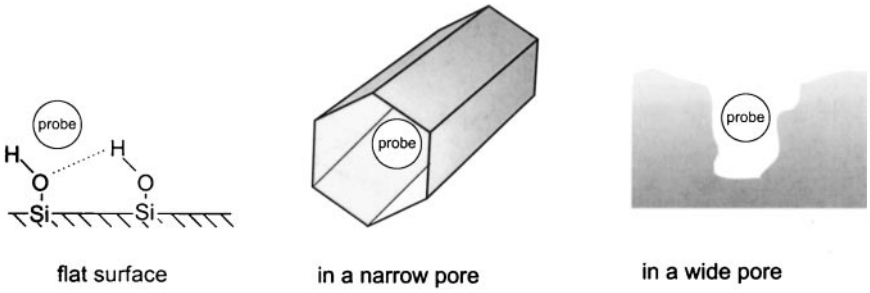
There exists still a problem in determining reasonable β values for bare silica and other moderately strong solid acids [13, 14, 31, 32]. For this purpose, different UV/Vis probes are suitable as long as their UV/Vis absorption maxima adequately reflect the β value of a surface environment [31]. However, this is not always accomplished for UV/Vis probes bearing primary amino groups such as



Scheme 1. Solvatochromic probe dyes used

4-aminobenzophenone [31, 32] and the aminobenzodifuranone dye (**5**) [14, 31, 33], because they do also interact with the lone electron pair of the nitrogen atom and/or the carbonyl oxygen and acidic sites of the surface. Because **5** has been found suitable as a HBA probe for synthetic polymers and solvents with HBA properties [19], its applicability as β indicator for some silica materials will be considered in this work. Nevertheless, the *Kamlet-Taft* parameters must be handled with caution in order to be mathematically orthogonal, and they neglect any other higher order term.

For the solvatochromic measurements, very low concentrations of the indicators are used to avoid multilayer adsorption on the surface. In the case of a mobile probe, the probe migrates to this site corresponding to a minimum of free energy (see Scheme 2). Using silica and weak basic probe molecules in organic liquids, it is assumed that the strongest acidic sites of the surface preferentially interact at low dye concentration, but the energies are average energies of all the sites to which the base coordinates [20, 34]. This average energy is a measure of the acid strength or



Scheme 2. Possible localizations of a solvatochromic probe on surface environments with different morphologies

polarity strength of the strongest site only if just the strongest site interacts. However, it is assumed that a freely accessible surface (particle or flat surface) does not restrict the mobility of a probe since the probe is well soluble in the liquid. The situation can change dramatically when the probe is adsorbed in a confined space (inside MCM-41) or encapsulated in a hydrogel or xerogel [34]. In this paper we will focus our interest to silica particles with different morphologies and pore size distribution where no confinement effects are expected, because a really solvent-like behaviour is only expected for freely accessible silica particle surfaces in a slurry where the solvents and the probe have enough available space and are not restricted in their thermal motion.

Therefore, it is of great interest to evaluate the relevance of the calculated polarity parameters α and π^* with regard to independent physicochemical parameters such as the catalytic activity of the solid acid catalyst, adsorption, and chromatographic properties [35–38]. *Park* and *Carr* have shown for the first time that the retention behaviour of solvents on a stationary silica phase is precisely determined by the HBA property (β term from Eq. (1)) and the dipolarity/polarizability (π^* term from Eq. (1)) of the solvents [35, 36]. It could also be shown that the rate of a polar reaction to be catalyzed by a moderately strong solid acid catalyst increases by increasing the α value of the solid acid [38]. These results clearly support the importance of the determined surface polarity parameters for practical applications. Furthermore, the linear correlation of the zeta-potential value measured in water with the β value determined in dichloromethane of organically functionalized silica particles shows the widespread conceptional background of the solvatochromic method for surface environments [14, 39].

The objective of the present review is the reinterpretation and critical reflection of some of our former results using an extended set of surface polarity indicators. Especially the influence of the structure of the probe (basicity and hydrophilicity) [29] and the suspending liquid on the α and π^* values for different silica samples will be discussed, because also weak HBA solvents, *i.e.* aromatics, halogenated solvents, or alkanes, can significantly change the surface reactivity of a solid acid [23, 38]. For this purpose, the established polarity indicators **1**–**5** have been selected (see Scheme 1). As suspending liquids we used weak HBA and moderately strong dipolar solvents. Their polarity parameters are given in Table 2.

Results

Influence of the structure of the probe on the surface polarity determined for bare silica

In several papers, various solvatochromic probes adsorbed on silica have been reported. Table 1 presents UV/Vis spectroscopic data for **1**–**4** and **5** when adsorbed on various silica samples.

Despite the silica samples altogether show quite the same overall surface polarity as expressed by their $E_T(30)$ value, they behave differently with respect to the probes **1**, **2**, **4**, and **5**. The corresponding polarity parameters α, β, and π^* calculated from Eqs. 5–8 for different probe pair combinations applied are compiled in Table 2.

It is obvious that the established probe pair **1** and **2** gives reasonable α and π^* values, whereas the probe pair **1** and **4** gives too large π^* and too low α values. We think that the bathochromic shift of the indicator **4** when adsorbed on silica contains

Table 1. UV/Vis absorption maxima of the indicator dyes **1**, **2**, **4**, and **5** when adsorbed on different silica samples from a 1,2-dichloroethane solution and related data for strong HBD solvents

Environment	$\nu_{max} \cdot 10^3/cm^{-1}$				$E_T(30)/kcal \cdot mol^{-1}$ (measured)
	1	**2**	**4**	**5**	
1,2-Dichloroethane (*DCE*)	16.39	28.25	23.75	17.42	41.3
Aerosil® 300/*DCE*	18.48	25.51	21.83	17.45	57.8
KG® 60/*DCE*	18.73	25.25	21.19	17.99	58.1
LC® 1500/*DCE*	18.98	25.13	21.51	17.48	58.5
Wacker silica[a]/*DCE*	18.69	25.25	21.93	19.42	–
2,2,2-trifluoroethanol	19.31	25.77	22.68	19.38	59.8
1,1,1,3,3,3-hexafluoro-2-propanol	20.04	24.94	21.98	20.04	65.3

[a] Nondried silica sample

Table 2. Calculated polarity parameters of four different silica samples utilizing ν_{max}(probe) of the probe pairs **1** and **2**, **1** and **4**, and **1** and **5**

Silica/solvent system	$\alpha(\mathbf{1},\mathbf{2})^a$	$\alpha(\mathbf{1},\mathbf{4})^b$	$\pi^*(\mathbf{1},\mathbf{2})^c$	$\pi^*(\mathbf{1},\mathbf{4})^d$	$\beta(\mathbf{1},\mathbf{5})^e$
Aerosil 300®/*DCE*	1.01	−0.06	1.09	2.62	0.50
KG 60/*DCE*	1.11	−0.24	1.11	3.13	0.36
LC 1500/*DCE*	1.22	0.03	1.09	2.81	0.57
Wacker silica/*DCE*	1.10	0.08	1.12	2.50	−0.12

[a] Calculated by means of Eq. (5) ($\alpha = -7.900 + 0.453\nu_{max}(\mathbf{1}) \cdot 10^{-3} + 0.021\nu_{max}(\mathbf{2}) \cdot 10^{-3}$);
[b] calculated by means of Eq. (7) ($\alpha = -19.146 + 0.489\nu_{max}(\mathbf{1}) \cdot 10^{-3} + 0.460\nu_{max}(\mathbf{4}) \cdot 10^{-3}$);
[c] calculated by means of Eq. (6) ($\pi^* = 13.889 - 0.251\nu_{max}(\mathbf{1}) \cdot 10^{-3} - 0.320\nu_{max}(\mathbf{2}) \cdot 10^{-3}$);
[d] calculated by means of Eq. (8) ($\pi^* = 24.632 - 0.181\nu_{max}(\mathbf{1}) \cdot 10^{-3} - 0.855\nu_{max}(\mathbf{4}) \cdot 10^{-3}$);
[e] calculated by $\beta = 3.059 + 0.174\nu_{max}(\mathbf{1}) \cdot 10^{-3} - 0.331\nu_{max}(\mathbf{5}) \cdot 10^{-3}$

too much contributions of the π^* term, because it shows an unprecedented large bathochromic shift which is similar to the effect observed in *HFI* (1,1,1,3,3,3-hexafluor-2-propanol). May be probe **4** responses to a higher order term. However, the dubious results for the pair **1** and **4** show a general problem: is it really justified to seperate the α and π^* term from two units of measurement? As a consequence of this conclusion, the concept for determining rigid parameters for surface environments has to be abandoned. In a following paper we will discuss this important question again.

Using probe **5** as β indicator, the silica surface would exhibit a moderately strong HBA property with similar strength compared to tetrahydrofuran or acetonitrile. This is not reasonable, because silica becomes not protonated even by strong acids like CF_3SO_3H [40]. Furthermore, a β value of 0.4 for silica does not correspond to its isoelectric point from zeta-potential measurements [14, 39]. Therefore, we assume that **5** is adsorbed *via* the carbonyl oxygen atom on silica and not *via* the hydrogen atom of the amino group. In a following paper we will make use of **5** as indicator for several solids and discuss this point again, because one silica batch shows a reasonable β value with **5** as indicator.

Influence of the solvent property on the surface polarity of bare silicas

For investigating the influence of the solvent on the polarity of the silica/solvent interface, we have chosen Aerosil® 300 and the porous silica KG® 60 which show very similar catalytic activity and surface polarity parameters in 1,2-dichloroethane as solvent [23, 38]. Unfortunately, the iron complex **1** is insoluble in weak dipolar solvents such as hexane, cyclohexane, toluene, benzene, tetrahydrofuran, dioxane, or anisole [27]. The problem can be circumvented when **1** is adsorbed on the silica sample from a dichloromethane solution and the coloured silica is filtered and dried [41]. The silica sample with the adsorbed dye **1** is suspended in this solvent where **1** is insoluble. This is indicated in Table 3 for **1** on silica with an asterisk. However, probe **1** is then restricted in its naturally occuring motion which has to be taken into account when interpreting the results. In moderately and stronger polar solvents, in particular the indicators **2**, **3a**, and **4** adsorb weakly on silica. Therefore, sometimes the difference between the UV/Vis spectrum in the slurry from and that in the supernatant solution has been utilized. This is specifically indicated in the Table 3. When **1** adsorbs from 1,2-dichlorethane on silica, a characteristic change of colour from blue (supernatant solution) to red (silica surface) is observed. The supernatant solution remains colourless. The adsorption process of **2** or **3a** can be easily followed by the eye of the investigator. In toluene or 1,2-dichlorethane, the solution of **2** or **3a** is colourless; after adsorption on silica, a yellow colour appears on the surface. Figures 1a,b show UV/Vis spectra of the adsorbed polarity indicators **1** and **3b**, respectively, on Aerosil® 300 measured in various solvents.

1 does not adsorb on silica from strong HBD solvents such as *DMSO*, *DMF*, or N-methylpyrrolidone; similar results have been found for derivatives of *Michler*'s ketone. It should be emphasized, however, that the acid-sensitive indicator **1** does well adsorb from alcoholic solvents on the porous silica KG® 60, whereas the other indicators do not. On Aerosil® 300, no adsorption from alcoholic solvents has been observed.

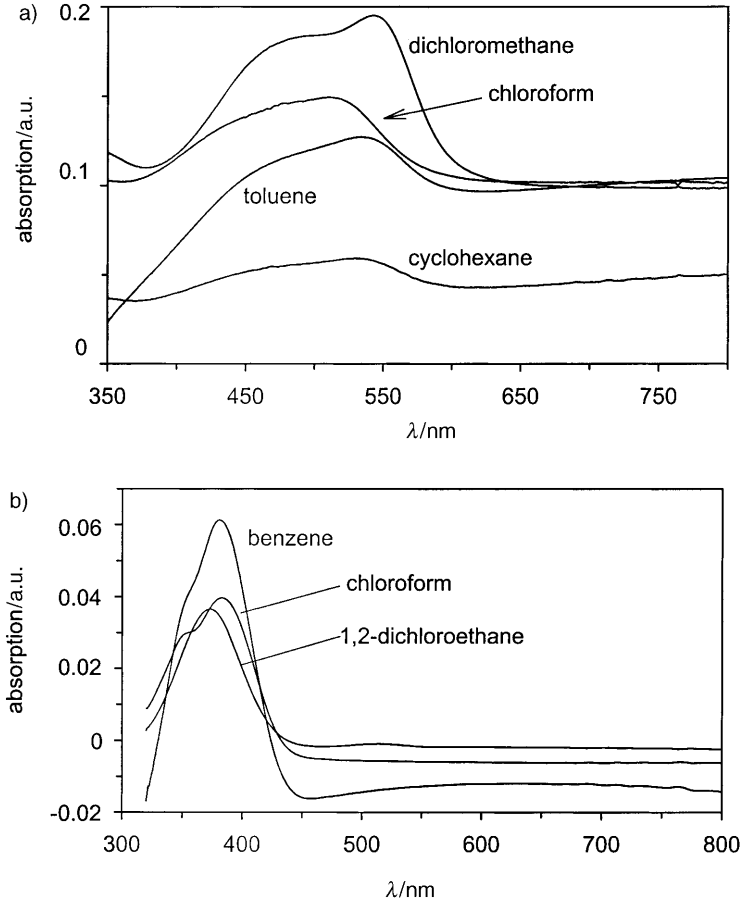


Fig. 1. a) UV/Vis absorption spectra of **1** adsorbed on Aerosil® 300 in dichloromethane, chloroform, toluene, and cyclohexane, respectively; the corresponding ν_{max} values are given in Table 3; b) UV/Vis absorption spectra of **3b** adsorbed on Aerosil® 300 in *DCE*, chloroform, and benzene, respectively; the corresponding ν_{max} values are given in Table 3

Surface polarity parameters of functionalized silicas

$E_T(30)$ values as well as UV/Vis absorption maxima of the indicators **1** and **2** when adsorbed on various organofunctionalized silica particles and solid acid catalysts have been reported [11, 23]. These data were taken in particular from Refs. [11] and [23] for the correlation analyses $E_T(30) = f(\alpha, \pi^*)$.

Discussion

The UV/Vis absorption of the acid sensitive surface polarity indicator **1** ($\nu_{max}(\mathbf{1})$) when adsorbed on Aerosil® 300 shows a significant bathochromic shift in increasing the basicity of the suspension solvent used. This is shown by Eq. (9a). Here and in the following, ν_{max} is expressed in cm^{-1}; r: correlation coefficient, *sd*: standard deviation, n: number of solvents, F: significance.

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 19.09 - 3.42\beta \quad (r = 0.91, sd = 0.39, n = 10, F < 0.0001) \quad (9a)$$

Table 3. UV/Vis absorption maxima ν_{max} of the probes **1**, **2**, **3a**, and **3b** when adsorbed on two different silica samples, KG® 60 (**S1**) and Aerosil® 300 (**S2**), respectively, in various solvents

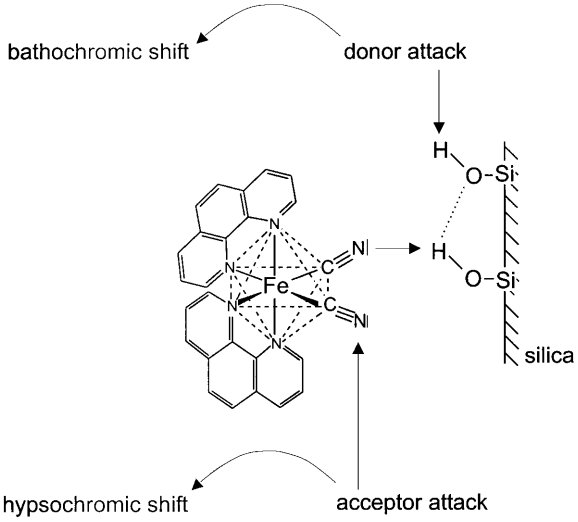
Solvent	α	β	π^*	$\nu_{max} \cdot 10^{-3}/cm^{-1}$					
				1		**2**		**3a**	**3b**
				S1	**S2**	**S1**	**S2**	**S2**	**S2**
CH_2Cl_2	0.13	0.10	0.82	18.55	18.42	25.45	25.38	25.77	26.32
$CHCl_3$	0.20	0.10	0.58	18.52	18.42	25.58	25.58	25.84	26.04
Toluene	0	0.11	0.54	18.73*	18.76*	25.51	25.64	25.91	26.46
CCl_4	0	0.10	0.28	18.76*	b	26.53	26.53	26.11	d
Cyclohexane	0	0	0	18.52*	18.87*	26.32	26.18	d	d
DMF	0	0.69	0.88	b	16.20[e]	a/b	a/b	a/b	a/b
THF	0	0.55	0.58	17.57	17.70[e]	a	a/b	a	b
CH_3NO_2	(0.22)	0.06	0.85	18.73	18.80[e]	c	c	b/c	b/c
CH_3CN	0.19	0.40	0.75	b	18.00[e]	b	b	a	a/b
$ClCH_2CH_2Cl$	0	0.10	0.81	18.69	18.80	25.32	25.51	25.77	26.74
C_6H_6	0	0.10	0.59	b	19.44[e]	b	b	26.18	26.18
MeOH	0.93	0.62	0.60	18.42	a	a	a	a/b	a/b
EtOH	0.83	0.77	0.54	18.21	a	a	a	a/b	a/b
TFE	1.51	–	0.73	19.16	b	a	b	a/b	a/b
HFI	1.96	–	0.65	18.87	b	a	b	a/b	a/b
Acetone	0.08	0.43	0.71	17.86	b	a	a	a/b	a/b
Diethyl ether	0	0.47	0.27	17.70*	17.45*	26.04	a/c	29.15	29.15
n-Hexane	0	0	−0.04	18.42*	b	26.32	b	d	d
p-Xylene	0	0.12	0.43	b	b	b	b	25.91	26.25
$Cl_2CHCHCl_2$	0	0	0.95	b	b	b	b	26.32	26.60

[a] No adsorption; [b] not measured; [c] detection not possible; [d] probe is insoluble in the pure solvent; [e] taken from Ref. [42]; for *DMF* and CH_3CN, the UV/Vis spectrum of **1** on the surface interferes with that of the surrounding solution; * asterisks denote that **1** is adsorbed on silica from a *DCM* solution; then the silica sample has been dried and measured in the solvent indicated

This result is reasonable, because the acid-base interactions of the silanol groups with the solvent play an important role [42–45]. The nucleophilic attack of the lone electron pair of the solvent on the silanol groups decreases the hydrogen-bond donating capacity of the silica surface and thus the interacting strength with the probe molecule. This leads to a bathochromic shift of the UV/Vis absorption band of the adsorbed indicator **1**. The solvatochromic UV/Vis absorption band of **1** ($\nu_{max}(\mathbf{1})$) in well-behaving regular solvents shows a hypsochromic shift upon increasing the α and π^* value ($a = 2.24$ and $s = 1.63$ according to Eq. (2)) of the solvent [27, 28]. Using multiple correlations of $\nu_{max}(\mathbf{1})$ (on silica) with α, β, and π^*, the quality of the correlation is not improved, but the significance decreases.

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 19.14 - 3.40\beta - 0.08\pi^* \quad (r = 0.91, sd = 0.41, n = 10, F = 0.0008) \qquad (9b)$$

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 19.14 - 1.05\alpha - 3.53\beta + 0.07\pi^* \quad (r = 0.91, sd = 0.46, n = 9, F = 0.01) \qquad (11c)$$



Scheme 3. Multiple interactions of Fe(*phen*)$_2$(CN)$_2$ with silanol groups and solvent molecules

The result of Eq. (9a) is in accordance with values from the literature, *i.e.* the silanol valency vibration of silica decreases with increasing *Gutmann* donor number (*DN*) of the solvent used [46]; *DN* and β correlate well with each other [3]. Because the correlation of $\nu_{max}(\mathbf{1})$ with the acceptor number (*AN*) of the solvent is also well established [27, 28, 47, 48], it seems obvious that the acid-base interaction between the silanol groups and the lone electron pair of the solvents plays the major role. Possible interactions of **1** with silica and the solvents are suggested in Scheme 3.

For *Michler*'s ketone as polarity indicator when completely adsorbed on silica in a suitable solvent, the best fit has been found for the influence of the π^* term on $\nu_{max}(\mathbf{2})$ (Eq. (10)).

$$\nu_{max}(\mathbf{2}) \cdot 10^{-3} = 26.40 - 1.19\pi^* \quad (r = 0.84, sd = 0.27, n = 5, F = 0.04) \qquad (10)$$

However, for **2** adsorbed on Aerosil® 300, only five solvents could be cleanly measured, and the significance of this relation is insufficient for a profound interpretation. A multiple correlation analyses also makes no sense for this series.

For the adsorbed hydrophilically substituted *Michler*'s ketone derivative **3a**, a significant influence of the β term of the solvent upon the UV/Vis absortion maximum has been found.

$$\nu_{max}(\mathbf{3a}) \cdot 10^{-3} = 25.33 + 7.51\beta \quad (r = 0.92, sd = 0.46, n = 8, F = 0.0005) \qquad (11a)$$

$$\nu_{max}(\mathbf{3a}) \cdot 10^{-3} = 24.85 + 8.25\beta + 0.65\pi^* \quad (r = 0.92, sd = 0.48, n = 8, F = 0.003) \qquad (11b)$$

$$\nu_{max}(\mathbf{3b}) \cdot 10^{-3} = 25.81 + 6.61\beta \quad (r = 0.91, sd = 0.44, n = 7, F = 0.001) \qquad (12a)$$

$$\nu_{max}(\mathbf{3b}) \cdot 10^{-3} = 24.17 + 9.17\beta + 2.07\pi^* \quad (r = 0.96, sd = 0.33, n = 7, F = 0.002) \qquad (12b)$$

$$\nu_{max}(\mathbf{3b}) \cdot 10^{-3} = 24.28 - 2.57\alpha + 8.96\beta + 2.10\pi^* \quad (r = 0.98, sd = 0.26, n = 7, F = 0.003) \quad (12c)$$

$\nu_{max}(\mathbf{3a})$ as well as $\nu_{max}(\mathbf{3b})$ reflect mainly the dipolarity/polarizability and the HBD capacity of well-behaving regular solvents [29]. However, it is shown by Eq. (9a) that the HBA property of the solvent has a significant influence upon the surface acidity. Thus, since the α value of silica decreases, $\nu_{max}(\mathbf{3a})$ and $\nu_{max}(\mathbf{3b})$ shift hypsochromically which is indicated by the positive sign of the coefficient for the β term in Eqs. (11a), (11b), and (12a–c). It seems that the additional polar alcoholic groups at the dimethylamino substituent are responsible for significant acid-base interactions with the silica surface compared to the nonsubstituted **2**. The shift of $\nu_{max}(\mathbf{3a})$ as well as $\nu_{max}(\mathbf{3b})$ for adsorbed **3a** and **3b**, respectively, is also in accordance with a strong acid-base interaction for these two adsorbed hydrophilic probes with silica. The influence of the terms α and π^* of the solvents on $\nu_{max}(\mathbf{3a})$ and $\nu_{max}(\mathbf{3b})$ play a less important role. This shows that the solvatochromic response of **3a** and **3b**, respectively, preferentially reflects the solvent influences on the acid-base interaction with silica and not the (intrinsic) solvatochromic property of the probe, whereas for **2** – which seems to be weaker adsorbed – the direct solvent influence on the probe itself is reflected. This result is very important for a correct interpretation of sorptio-solvatochromatic effects of adsorbed probes on surfaces.

For KG® 60, the following correlations have been found for the adsorbed polarity indicators **1** and **2** (the probe dyes **3a** and **3b** have not been considered for this material so far).

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 18.32 + 0.31\alpha \quad (r = 0.44, sd = 0.41, n = 14, F = 0.10) \quad (13a)$$

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 18.63 - 1.02\beta \quad (r = 0.67, sd = 0.31, n = 12, F = 0.01) \quad (13b)$$

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 18.29 + 0.30\pi^* \quad (r = 0.19, sd = 0.45, n = 14, F = 0.50) \quad (13c)$$

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 18.50 - 1.09\beta + 0.29\pi^* \quad (r = 0.70, sd = 0.32, n = 12, F = 0.33) \quad (13d)$$

The correlation equations (13a–d) gave no specific hint at a prefered silica/solvent interaction. Hence, for the porous silica a rather complex influence of the surrounding solvent upon the surface acidity seems to be operative. This is shown by the multiple correlation of $\nu_{max}(\mathbf{1})$ with α, β, and π^* (Eq. (14)) which shows sufficient significance and a satisfying correlation coefficient.

$$\nu_{max}(\mathbf{1}) \cdot 10^{-3} = 18.58 + 1.00\alpha - 1.85\beta + 0.17\pi^* \quad (r = 0.92, sd = 0.19, n = 12, F = 0.0007) \quad (14)$$

However, the HBA property of the solvents (β term or *DN*) mainly also decreases the HBD capacity (or *AN*) of the silica surface compared to Aerosil® 300 (Eq. (9a)). The influence of the π^* term is of minor importance but cannot be neglected. The influence of the α term is probably caused by the adsorbed HBD solvent molecules according to Scheme 3.

For the adsorption of **2** on KG® 60, a similar influence of the π^* term upon $\nu_{max}(\mathbf{2})$ is detectable as found for Aerosil® 300 (Eq. (15)).

$$\nu_{max}(\mathbf{2}) \cdot 10^{-3} = 26.40 - 1.26\pi^* \quad (r = 0.89, sd = 0.23, n = 7, F = 0.003) \quad (15)$$

It seems that the strength of adsorption of the probe molecule (P) on the surface determines the influence of the property of the solvent on the direction of the sorptio-solvatochromic UV/Vis shift of $\nu_{max}(P)$ according to Eq. (2). If the probe is more hydrophobic, the interaction with the evident hydrophilic bare silica surface environment is lowered. A similar result has been found for hydrophobically substituted nitroaniline derivatives as probes for micelle polarity [49].

Functionalized silica particles and other solid acids

For probing the well-established relationship $E_T(30) = f(\alpha, \pi^*)$ [2, 3] including an extended data set of organofunctionalized silicas and various solid acids [11, 23], we used α and π^* values determined by the probe pair **1** and **2** as well as directly measured $E_T(30)$ values by means of *Reichardt*'s betaine dyes. The result of the least squares analysis is given in Eq. (16) and Fig. 2.

$$E_T(30) = 40.68 + 11.45\alpha + 3.86\pi^* \quad (r = 0.86, sd = 1.98, n = 45, F < 0.0001) \qquad (16)$$

The correlation is only satisfactory which shows that the respective probe reflects the hydrogen bond acidity (α term) and dipolarity/polarizability (π^* term) of each surface environment differently in a certain section of the polarity scale. As a whole, the correlation is significant and shows, as expected from our former interpretations [11, 27], that the α term contributes stronger to $E_T(30)$ than does the π^* term [11, 19, 23]. However, we think that a systematic study using well defined solvatochromic probes concerning their basicity and hydrophobicity [49, 50] is necessary in order to evaluate the reliability of the parameters. At this time, the determined parameters are of practical relevance for specific applications.

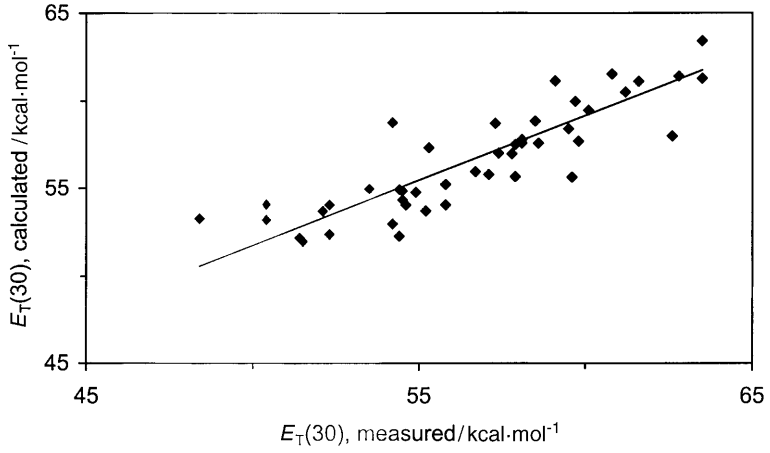


Fig. 2. Calculated *vs.* measured $E_T(30)$ values for organofunctionalized silicas and various solid acids including silicas, aluminas, titanium dioxides, and aluminosilicates; all data were taken from Refs. [11] and [23]

Conclusions

The interaction of a solvatochromic probe with a surface environment in a solvent can be well measured by the UV/Vis shift of the adsorbed polarity indicator when adsorbed on silica in transparent slurries. The quantitative adsorption of the probe dye requires specific conditions because the solvent competes with the probe. Therefore, unambiguously measurable UV/Vis absorption maxima of the adsorbed probe dye cannot be measured for each solvent used. It seems that a basic requirement is that the probe should be less basic than the solvent used for the silica slurry. Acid-base interactions between the probe and the silica surface predominate as shown by the correlation analyses of $\nu_{max}(\text{probe})$ – measured on the surface in the slurry – with the *Kamlet-Taft* solvent parameters of the solvent. It can be shown that not only the chromophoric system of the dye is responsible for the UV/Vis response of the respective interaction, but that the hydrophilicity or rigidity of the probe is also of importance. Therefore, the silica surface can be treated like a smooth solvent shell which mediates preferential HBD solvation. As a consequence of this research, polarity parameters for silica and solid acids are dynamic quantities.

At this moment, an interpretation of the results in terms of morphological reasons is too speculative. We think this is an important topic for future work, because the morphology of silica seems of importance for the interaction with both probe and solvent.

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Experimental

Chemicals

Fe(*phen*)$_2$(CN)$_2$ was prepared according to *Schilt* [51]. *Michler*'s ketone was purchased from Merck (Darmstadt), recrystallized twice from EtOH, and carefully dried before use. The hydrophilically substituted derivatives of **2**, **3a** and **3b**, were synthesized as previously published [29]. Coumarin dye 153 (**4**) was purchased from Radiant Dyes Laser Accessories GmbH. The aminobenzodifuranone dye (**5**) was kindly provided by BASF, Manchester. 1,1,1,3,3,3-hexafluor-2-propanol (*HFI*) and 2,2,2-trifluoroethanol (*TFE*) were used without further purification. All other solvents were dried and freshly distilled before use. The physical properties of the silica batches used in this study are given in Table 4.

Table 4. Physical properties and sources of the solid acids used in this work

Solid acid sample	BET-surface area (m^2g^{-1})	Specific pore volume (cm^3g^{-1})	Average pore diameter (nm)	Source
SiO_2, Aerosil 300®	240	–	–	Degussa
SiO_2, KG 60®	423	0.63	9.0	Merck
SiO_2, KG LC 1500®	30	–	5.5	Grace
SiO_2	200	–	–	Wacker

UV/Vis measurements

The UV/Vis absorption maxima of the dyes **1–5** adsorbed on the solid acid catalyst were recorded using a diode array spectrometer with glass fiber optics. The solid acids were heated at 400°C for 12 h. After cooling to room temperature under dried argon, a solution of the probe dye in the corresponding solvent (about 10^{-5} mol/dm^3) was added to the solid material. Care must be taken to avoid overloading the surface with the indicator used, as multilayer adsorption is expected in solution at higher concentrations as well as interfering absorptions from the nonadsorbed dye from the solution.

For the UV/Vis measurement of transparent slurries, the amount of the solid acid silica must be limited in order to achieve a sufficient particle concentration in the continuously stirred slurry. 0.1 to 0.2 g of silica in 15 cm^3 of the solvent are very suitable, but a lower amount is also possible. The amount of the silica portion has no influence on the position of the UV/Vis absorption maximum of the adsorbed probe dye.

The equipment employed was a UV/Vis spectrometer MCS 400 connected to an immersion cuvette TSM 5A (Zeiss). The measurement of the UV/Vis spectrum of the supernatant solution is possible in the same cell after the solid has deposited.

The measurements of silica particle suspensions are advantageous because they can be performed under inert conditions and reflect better the conditions suitable for liquid chromatography and catalysis in organic solvents. The reproducibility of the UV/Vis spectra of the adsorbed dyes is very good. For silicas, transparent suspensions are obtained in most liquids. This allows to record very good quality transmission spectra with an excellent reproducibility of less than $\lambda_{max} \pm 1$ nm. The position of the UV/Vis absorption maximum of the adsorbed dye on the silica particles remains constant during 1–2 h (*vide infra*).

Determination of the polarity parameters

The following dual correlations according to Eq. (4) have been used for the determination of the surface polarity parameters [19, 30]. $\alpha(\mathbf{1},\mathbf{2})$ denotes that the solvatochromism of the indicators **1** and **2** has been considered in the multiple square analyses for this equation and that the influence of $\nu_{max}(\mathbf{1})$ on α dominates, because the coefficient a_1 for $\nu_{max}(\mathbf{1})$ is significantly larger than a_2 for $\nu_{max}(\mathbf{2})$ according to Eq. (4). Equations (5) and (6) were taken from Ref. [19], Eqs. (7) and (8) from Ref. [30].

$$\alpha(\mathbf{1},\mathbf{2}) = -7.90 + 0.45 \cdot \nu_{max}(\mathbf{1}) \cdot 10^{-3} + 0.02 \cdot \nu_{max}(\mathbf{2}) \cdot 10^{-3} \quad (r = 0.95, sd = 0.17, n = 34, F = 0.00) \quad (5)$$

$$\pi^*(\mathbf{2},\mathbf{1}) = 13.89 + 0.251 \cdot \nu_{max}(\mathbf{1}) \cdot 10^{-3} - 0.32 \cdot \nu_{max}(\mathbf{2}) \cdot 10^{-3} \quad (r = 0.57, sd = 0.15, n = 36, F = 0.00) \quad (6)$$

$$\alpha(\mathbf{1},\mathbf{4}) = -19.15 + 0.46 \cdot \nu_{max}(\mathbf{4}) \cdot 10^{-3} + 0.49 \cdot \nu_{max}(\mathbf{1}) \cdot 10^{-3} \quad (r = 0.98, sd = 0.09, n = 18) \quad (7)$$

$$\pi^*(\mathbf{4},\mathbf{1}) = 24.63 - 0.85 \cdot \nu_{max}(\mathbf{4}) \cdot 10^{-3} - 0.18 \cdot \nu_{max}(\mathbf{1}) \cdot 10^{-3} \quad (r = 0.94, sd = 0.08, n = 18) \quad (8)$$

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