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ORIGINAL CONTRIBUTION

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On the determination of polarity parameters of silica by means of solvatochromic probe dyes

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Abstract Empirical "solvent" parameters of silica surfaces are determined by means of solvatochromic dyes, e.g., $Cu(tmen)(acac)^+ ClO_4^-/B(C_6H_5)_4^-$, $Fe(phen)_2(CN)_2$, and Michlers Ketone dissolved in 1,2-dichloroethane or cyclohexane. The values obtained by UV/VIS-measurements are compared with both the polarity scales of Kamlet and Taft and with Gutmann's donor and acceptor numbers. Kamlet and Taft's α-parameter (the hydrogen-bond donation capacity of a solvent) is determined independently by means of salicylideneaniline. The π^*-parameter of silica is determined using 5-N,N-dimethylamino-5′-nitro-2,2′-bithiophene and the complex of tetracyanoethylene with Michlers Ketone, respectively. Further on the reliabilities of the obtained Kamlet-Taft parameters α, β, and π^* are checked by comparism with experimental and calculated values of the $E_T(30)$-parameter of silica by means of multi-parameter regression analysis. The surface properties of silica are influenced mainly by HBD-properties α (75%) and dipolarity/polarizability π^* (20%), but hardly by the HBA-properties β (< 5%). UV/VIS-measurements were carried out in a special equipment with glass fiber optics. A drawing of the apparatus is given.

Key words Acidity – basicity – dipolarity – silica – polarity – solvatochromic dyes – acceptor numbers – donor numbers

Introduction

Recently, we applied suspensions of aerosil in hexane and 1,2-dichloroethane (DCE) as reaction media and catalysts in Friedel–Crafts reactions [1]. It is of considerable interest to understand the parallels among electrophilic reactions carried out in solvents or on silica surfaces as reaction media [1, 2]. Therefore the nature of the silica surface requires further investigations in terms of its acidity, solvent polarity and its donor and acceptor properties. Several papers on these topics appeared during recent years [3–7]. The term "surface polarity" describes a very complex physico-chemical property whose definition is still controversial [4–6]. On the other hand, the solvent polarity is a complex quantity, too, but is well understood. It is currently impossible to describe all properties of a solvent by means of a single quantity, thus empirical parameters have been introduced to circumvent this fundamental problem. Empirical parameters are based on well defined solvent dependent processes like certain chemical reactions, shifts in NMR-signals of selected

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compounds, or, very conveniently, on solvatochromic effects shown by certain dyes. A discussion and a review on these topics is given in [8]. The polarity scales used most frequently to describe the nature of a medium are based on solvatochromic processes [8a]. Thus, we decided to apply the concepts well known from solvent polarity to silica surfaces [8b]. Well established scales are the $E_T(30)$-solvent parameter of Reichardt [8] and the donor numbers (DN) and acceptor numbers (AN) of Gutmann [9]. These polarity scales are based on well defined reference processes [8]. Unfortunately, all these empirical parameters reflect only a limited number of solvent properties. To circumvent the problems deriving from these limitations multi-parameter approaches have been introduced [8]. Among these multi-parameter approaches, that of Kamlet and Taft is used most. The linear solvation energy relationship (LSER) of Kamlet and Taft describes the influence of the Lewis acidity (α), the Lewis basicity (β), and dipolarity/polarizability (π^*) of a solvent upon the result of a chemical process (XYZ) in relation to the standard process $(XYZ)_0$ [10]. The LSER-multi-parameter approach of Kamlet and Taft is commonly written in the form:

$$(XYZ) = (XYZ)_0 + a\alpha + b\beta + s\pi^* \; . \qquad (1)$$

The solvent parameters α, β, and π^* are averaged values derived from numerous solvent dependent chemical processes [10]; a, b and s are coefficients.

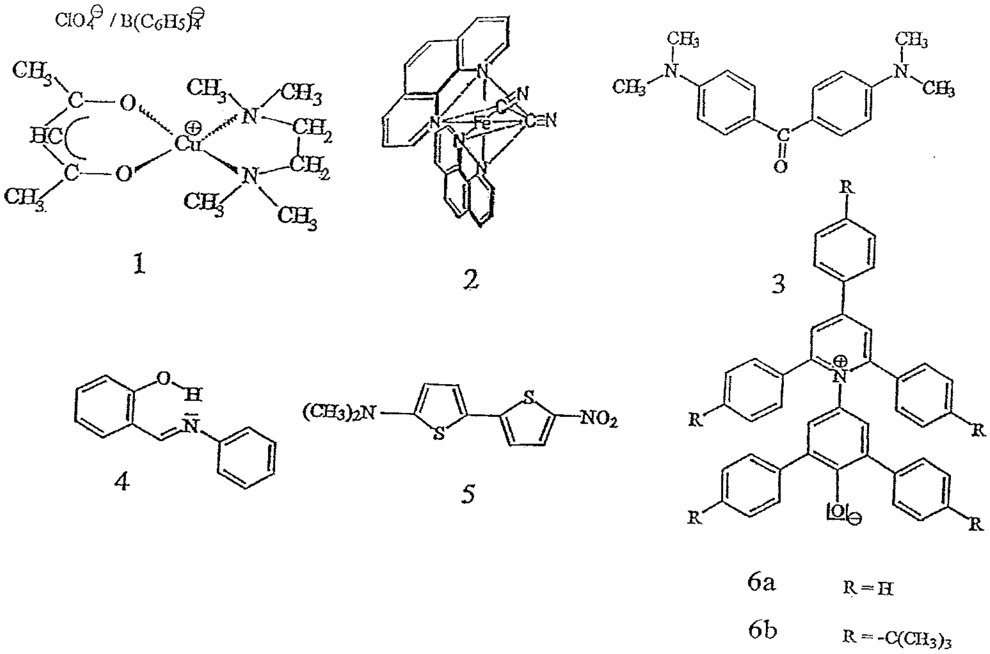
Leffler et al. were the first to report values for the α, β, and π^*-parameters of silica [6]. The authors used six different probes to estimate the value of the π^*-parameter of silica. The following values for a selected silica sample were yielded: 4.00, 2.68, 2.21, 1.70, 1.20, and 0.81, respectively, using 1-ethyl-4-nitrobenzene ($\beta = 0.31$), 4-nitroanisole ($\beta = 0.35$), 4-(N,N-dimethylamino) benzophenone, 4-methoxy-β-nitrostyrene, N,N-diethyl-4-nitroaniline ($\beta = 0.43$), and N,N-diethyl-3-nitroaniline ($\beta = 0.45$) as indicators (all π^*-values are taken from ref. [6]). The β-values of the indicators (in parenthesis) are taken from ref. [11]. The results show that the calculated values of the "π^*"-parameter of silica decrease as the basicity (β) of the probe dyes increases. The occurrence of acid-base interactions was not considered in the discussion by Leffler et al. [6]. The differences were discussed in terms of various adsorption sites on silica. The influence of acid-base interactions upon the spectral shift (π-π^*-transition) of the adsorbed indicator is interpreted in terms of different interaction mechanisms. Van-der-Waals forces are mainly reflected by the π^*-parameter and acid-base interactions by the α-parameter. Therefore determination of the π^*-parameter values applying a one parameter equation ($\nu_{\mathrm{i,max}} = \nu_{\mathrm{i,0}} + \tilde{s}_{\mathrm{i}}\pi^*_{\mathrm{i}}$ from ref. [6]) seems to be unsuitable for acidic surfaces. For example, N,N-diethyl-4-nitroaniline is protonated at the amino group in solution and the hypsochromic shift caused would result in a decrease in the π^*-value. On the other hand, in the gas phase the protonation exclusively takes place at the nitro group resulting in a bathochromic shift causing an increase in the π^*-value [12]. Both attacks, the protonation at the amino group and at the nitro group of the probe dye, can occur at the surface of silica. 1-Ethyl-4-nitrobenzene can be attacked only at the nitro group by the silanol groups, thus, the obtained value of the π^*-parameter is too high. The same problem goes for the determination of the α- and β-parameters of acidic surfaces by similar probe dyes bearing two different functional groups, e.g., nitro and amino. For this reason, reasonable values of surface polarity parameters can be obtained only if the probe dyes undergo well defined interactions with the surface groups. Furthermore, only such probe dyes are suitable which have been carefully characterized in terms of their acid-base and polarity behavior in both HBD- and HBA-solvents.

The Kamlet–Taft equation (1) may also be used to describe the relation of the amount of the solvatochromic shift (XYZ) of a probe dye and the solvent properties α, β, and π^* [7, 13]. Unfortunately, there are only a few statistically supported multiparameter approaches for probe dyes showing a sufficient relation of the amount of the solvatochromic shift ($\Delta\nu \approx 5000\ \mathrm{cm}^{-1}$) and the parameters α, β, and π^* exhibiting a high correlation coefficient ($r \geq 0.97, n > 30$). Both values of parameters α and π^* of silica were calculated simultaneously utilizing the two parameter approaches of the iron complex $\mathrm{Fe(phen)_2(CN)_2}$ and Michlers Ketone as probe dyes as reported in ref. [7a]. The values obtained with both indicators correlate very well to the α- and π^*-parameters over a wide solvent polarity range including HBD- and HBA-solvents as well [7b]. This correlation is described mathematically by a two-parameter equation:

$\nu_{\max} = a\alpha + s\pi^* + c$ [7a], with $a = 2.24$, $s = 1.63$, $c = 14.94$, and $a = -1.79$, $s = -2.18$, $c = 30.03$ for $\mathrm{Fe(phen)_2(CN)_2}$ and Michlers Ketone, respectively. Marcus employed the same concept for the determination of π^*- and α-parameters for solvent mixtures [13]. In ref. [7] we introduced only the methodical procedure and no discussion was given upon the surface properties of silica. The probe dye indicators $\mathrm{Fe(phen)_2(CN)_2}$ and Michlers Ketone adsorbed at silica were measured in a suspension of 1,2-dichloroethane. In the case of $\mathrm{Fe(phen)_2(CN)_2}$ the interaction with the surface groups proceeds via the cyano group and in the case of Michlers Ketone via the carbonyl oxygen and the aromatic ring [7b].

In our findings the contribution of the hydrogen-bond donating capacity α to the overall surface polarity exceeds the influence of the dipole–dipole interactions represented by the π^*-values. Our results for unmodified silica are in contrast to the findings reported in ref. [6]. Are these

Scheme 1 Probe dyes for measuring the surface polarity of silica



differences caused by the experimental method applied or are other fundamental reasons responsible for this contradiction? We assume that the overall surface properties of silica, α, β and π^*, are specifically influenced by the suspending solvent in which the probe dye and silica sample are measured. We found that the use of moderate HBA-solvents (ethers or ketones) modifies the surface acidity of silica thus influencing the α- and the π^*-values [14].

The objective of this paper is to determine reliable sets of values of 'solvent' parameters of silica surfaces, α, β, π^*, AN and DN, by means of well characterized probe dyes. The following compounds were selected as indicators for "surface" polarity (Scheme 1).

The specific solvatochromic properties of each indicator are discussed later. We employed special equipment with glass fiber optics to measure directly the UV/VIS-absorption of the adsorbed indicator in the suspending liquid. The measurement of aerosil in a transparent suspension of 1,2-dichloroethane allows to take UV/VIS-transmission spectra instead of the less easily performed measurements using the reflectance technique [6].

Experimental part

Aerosil 300 (Degussa) was heated at 423 K for 6 h under vacuum (< 1 Torr) prior to use. All experiments were carried out under an atmosphere of dry argon. The suspension of aerosil in 1,2-dichloroethane is sufficiently transparent and allows to take transmission spectra in the visible part of the spectrum. Aerosil/cyclohexane suspensions are transparent, too. Therefore it is possible to take transmission spectra in the visible part of the spectrum similar to those taken in 1,2-dichloroethane. Taking transmission UV/VIS-spectra of suspensions of silica KG 60 from Merck is accompanied by a higher error due to the larger particles size of KG 60. Measurements were carried out with an MCS 400 UV/VIS-Spectrometer (Zeiss) equipped with the immersion cuvet TS 5A (Zeiss). A blueprint of this special device is shown in Fig. 1.

The immersion cuvet can be vertically shifted, which allows to compare the spectra of the suspension as well as of the supernatant solution.

Materials

The copper complexes Cu(tmen) $(acac)^+ClO_4^-$ and $B(C_6H_5)_4^-$ (1^+C^- and 1^+B^-), were prepared according to ref. [16].

N-Methylacridiniumiodid (NMA^+I^-) was prepared by refluxing acridine and methyliodide in isopropanol for 10 h. The product precipitated as red needles after cooling the reaction mixture in an ice bath. The crude product was recrystallized from isopropanol. The corresponding tetraphenylborate is obtained by mixing equal amounts of aqueous solutions of sodium tetraphenylborate and N-methylacridiniumiodide under stirring. The pale yellow

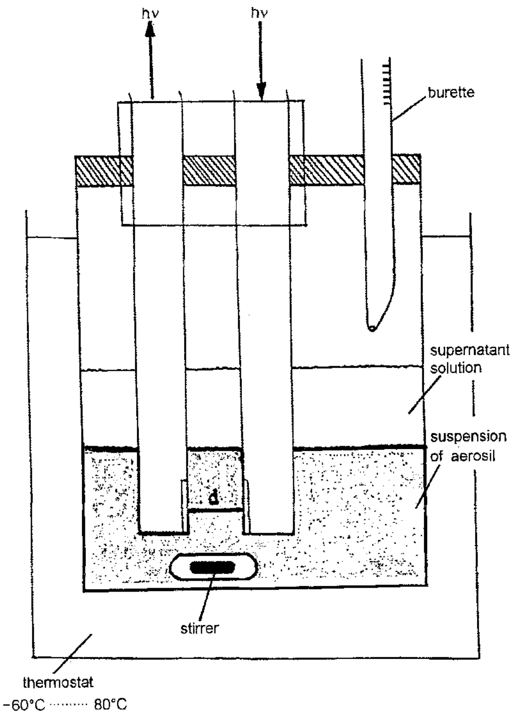


Fig. 1 Scheme of the cell for the UV/VIS-measurement of transparent aerosil suspensions with a diving cuvette under inert conditions; *d* is the optical distance (0.5 cm) of the cuvette

$NMA^+B(C_6H_5)_4^-$ precipitates quantitatively. Carefully washing with water and recrystallization from nitromethane yields yellow needles with accurate combustion analysis. Tetra-(*n*-butyl) ammonium perchlorate was obtained similarly by mixing a sodium perchlorate solution with tetra(*n*-butyl) ammonium bromide in water at 353 K. The tetra(*n*-butyl) ammonium perchlorate salt precipitates during slow cooling to room temperature. After drying in a desiccator (atmospheric pressure) over $CaCl_2$ small amounts for use were recrystallized from CH_2Cl_2.

$Fe(phen)_2(CN)_2$ (2) and Michlers Ketone (3) (Aldrich) were measured employing the same procedure as outlined above. An introduction to the mathematical treatment of the measured values is given in ref. [7]. Salicylideneaniline (4) was synthesized by the condensation of salicylaldehyde with aniline in methanol and subsequent recrystallization from the same solvent.

The 5-N,N-Dimethylamino-5′-nitro-2,2′-bis-thiophene (5) dye was kindly donated by F. Effenberger, University of Stuttgart.

The pyridinium-N-phenolate betaine dyes (6a, b) were a kind gift of Chr. Reichardt, University of Marburg. The solvents 1,2-dichloroethane and cyclohexane (Merck, Darmstadt) were distilled from CaH_2 prior to use.

1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,2-trifluorethanol, 2,2,2-trichloroethanol, 1,1,1-trichloroethane,1,1-dichloroethane and 1,1,2,2-tetrachloroethane (Aldrich) were UV-grade and were used without further purification.

Results and discussion

HBA-properties (DN and β-parameter)

The transition metal complex N,N,N,N-tetramethylethylene-acetylacetonato copper II perchlorate or -tetraphenylborate $[Cu(tmen)\,(acac)^+ClO_4^-$ or $B(C_6H_5)_4^-]$ (1^+C^- or 1^+B^-) [15, 16] shows a solvatochromism that is suitable for both the donor scale of Gutmann (Eq. (2a) according to [16]) as well as the β-scale of Kamlet and Taft (Eq. (2b) according to [17]).

$$DN = 195.5 - 0.0102\, \nu_{max}(1^+C^-) \tag{2a}$$

$$r = 0.990, \quad n = 12$$

$$\beta = 6.716 - 0.358\, \nu_{max}\,(1^+C^-)10^{-3} \tag{2b}$$

$$r = 0.960, \quad n = 17\,.$$

Unfortunately, the absorption coefficient of the forbidden *d-d**-transition of the copper complex is rather low, thus high surface concentrations of the complex are required to take UV/VIS-spectra. Our first experimental attempts failed to obtain sufficient surface concentrations of the copper complex by adsorption on dried silica (KG 60) samples. Solid, dried adsorbates of 1^+C^- or 1^+B^- at silica do not exhibit an absorption in the visible region which corresponds to the *d-d**-transition of 1^+C^- or 1^+B^-. However, the use of a concentrated solution of 1^+C^- yields a colored aerosil suspension in 1,2-dichloroethane, the supernatant liquid remains colorless. Comparison of the UV/VIS-spectra of the supernatant solution and of the suspension indicates an exclusive adsorption of the probe dye on the silica surface. Two questions arise: on which surface sites does 1^+ chemisorb and how does this reaction proceed?

Basically, two interaction mechanisms are possible:

I) The interaction of probe and surface proceeds via a counter ion bridge as evidenced for triarylcarbenium salts and other ion pairs [18]. In this case the Lewis acidity of the surface groups is responsible for the chemisorption.

II) The interaction proceeds directly by interaction of the oxygen of silanol- or siloxane surface groups with the copper atom of 1^+. In this case the Lewis basicity of the surface is responsible for the chemisorption.

The latter kind of interaction (II) is essential for the determination of reliable values of basicity parameters of silica. In spite of the distinct difference for the ability of forming hydrogen bonds like $X^- \cdots HO$- of the counter ions employed, $C^- \gg B^-$ [19], both salts, 1^+C^- and 1^+B^-,

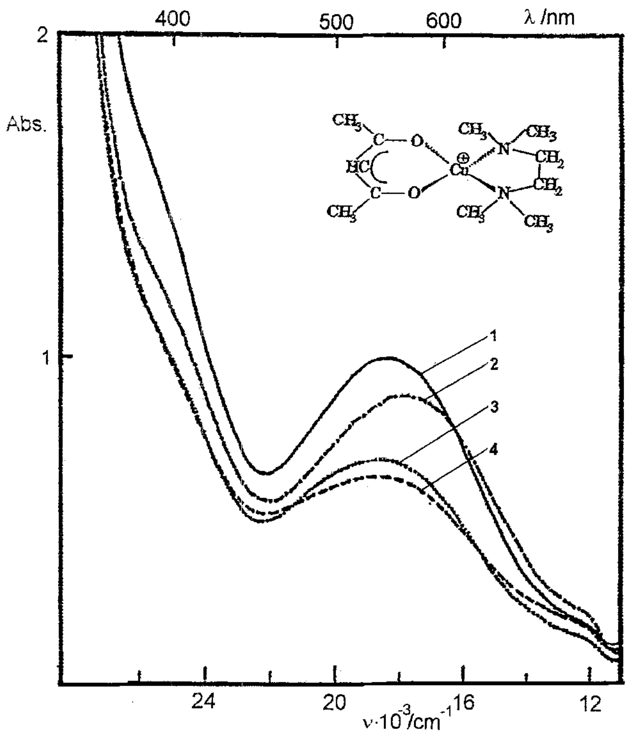
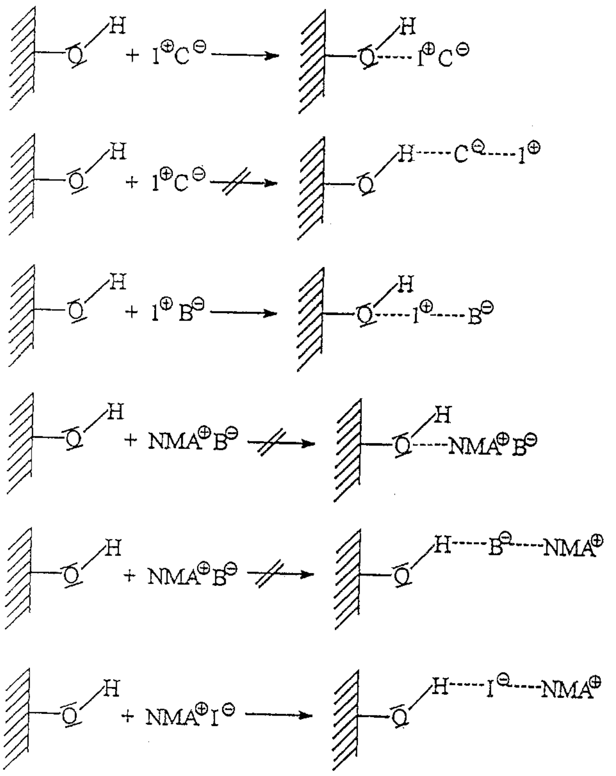


Fig. 2 UV/VIS-transmission spectra of Cu(tmen) (acac)$^+$ adsorbed at aerosil measured in 1,2-dichloroethane 1 ——— aerosil dried + Cu(tmen) (acac)$^+$ ClO_4^-, 2 - - - - - - aerosil dried + Cu(tmen) (acac)$^+$ $B(C_6H_5)_4^-$, 3 ··· ··· ··· aerosil nondried + Cu(tmen) (acac)$^+$ $B(C_6H_5)_4^-$, 4 — · — · — · — · — silica 60 + Cu(tmen) (acac)$^+$ ClO_4^-

show qualitatively the same UV/VIS-spectra of the suspension of 1^+ in aerosil /1,2-dichloroethane as shown in Fig. 2. This behavior demonstrates that the interaction of the cation 1^+ occurs directly via silica surface groups and not via an ion pair bridge [18]. The different behavior of C^- and B^- towards silica is proven by NMA^+ salts. The π-π^*-transition of the NMA^+ is monitored in the range of 22 000 and 30 000 cm^{-1}. The non-nucleophilic counter ion $B(C_6H_5)_4^-$ cannot mediate an interaction of the less electrophilic NMA^+. In contrast $NMA^\pm$ perchlorate or -iodide are adsorbed on silica. In these cases the adsorption occurs via the counter ion bridge (see Scheme 2). No characteristic qualitative changes in the UV/VIS-spectrum of the NMA^+ are observed between those in solution ($NMA^+ClO_4^-$) and of those measured at the surface of silica (NMA^+I^-). It is remarkable, that in 1,2-dichloroethane the internal CT-transition from iodide to NMA^+ observed at 20 200 cm^{-1} [20] is suppressed on silica surfaces due to the interaction of the iodide with silanol groups. The specific hydrogen bond between silanol and iodide increases the ionization potential of iodide [21].



Scheme 2 Simplified counter ion dependend interaction mechanism of NMA^+- and Cu(tmen) (acac)$^+$-salts with silica surfaces

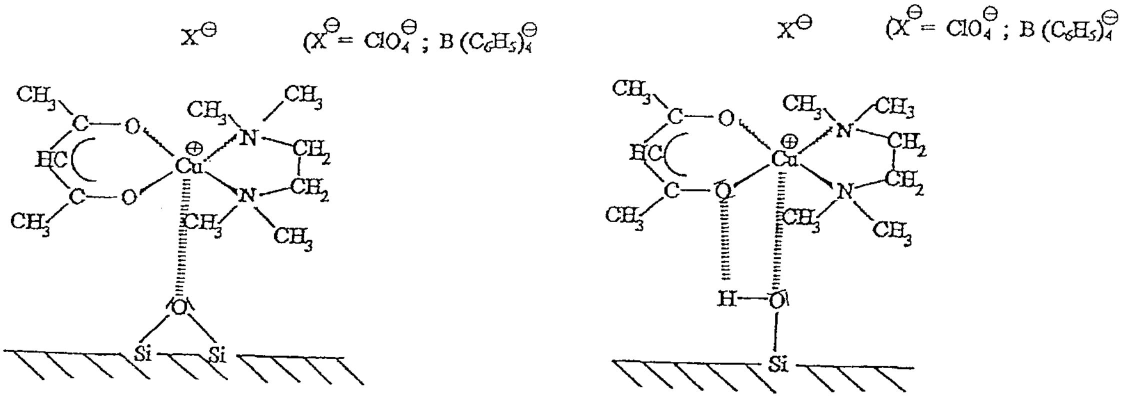
The basicity indicator 1^+C^- is not displaced from the silica surface in the presence of $(C_4H_9)_4N^+ClO_4^-$. In this case a very small bathochromic shift ($\Delta\nu < 200$ cm^{-1}) of the adsorbed 1^+ is observed. Thus, ClO_4^- as counter ion does not mediate the adsorption of 1^+ with silanol. The chemisorption mechanism of 1^+ should be very similar to the adsorption mechanism of bis (1,1,1,5,5,5-hexafluoroacetylacetonato) copper(II) on silica [22]. The detailed interaction mechanism supporting our mechanistic assumption was studied recently by FTIR-spectroscopy [22]. Two possible interaction mechanisms of adsorbed 1^+ at aerosil are suggested (Scheme 3).

The results reported in ref. [22] encouraged us to calculate values of donor parameters for silica by means of Eq. (2a) and Eq. (2b) using complex 1^+ as probe dye. The following $\nu_{\max(\text{d}-\text{d}^*-\text{transition})}$ values were obtained for the copper complex adsorbed on aerosil. Measurements were performed as suspensions in 1,2-dichloroethane.

sample 1: aerosil 300 dried at 573 K, with 1^+C^-, $\nu_{\max} = 18\,500$ cm^{-1}

sample 2: aerosil 300 dried at 573 K with 1^+B^-, $\nu_{\max} = 18\,600$ cm^{-1}

sample 3: aerosil 300 nondried with 1^+B^-, $\nu_{\max} = 18\,000$ cm^{-1} and



Scheme 3 Suggested interaction mechanism of Cu(tmen) (acac)$^+$ with silica surface groups

sample 4: silica (KG 60 from Merck) nondried with 1^+C^-, $\nu_{max} = 18\,100\ cm^{-1}$ (measured in stoppered cuvets).

Throughout, triple measurements have been carried out; the reproducibility was very good ($\Delta\nu < 100\ cm^{-1}$). This corresponds to an error in $\Delta\beta$, of $\pm$ 0.02 and in ΔDN to an error of $\pm$ 2. In the case of sample 4 the $\Delta\nu$-value approaches $\cong 150\ cm^{-1}$. As expected, the value of the donor activity or the Lewis-basicity of a dried silica surface is quite low ($\beta = 0.06 \pm 0.02$) and comparable to weak donor liquids like 1,2-dichloroethane or nitrobenzene. Nondried silica possesses a higher value for the Lewis-basicity ($\beta = 0.27$), which is evidently lower than that of bulk water ($\beta = 0.47$). This result is in accordance with Arnett, who reported on the calorimetrically measured adsorption enthalpy of different Broensted acids on silica [23]. The adsorption enthalpy of various Broensted acids on silica is relatively low and independent of the Broensted acid strength (CH_3COOH in comparison to CF_3SO_3H). Therefore an interaction of Broensted acids with silica in organic liquids does not result in protonated silanol groups. In contrast to that, the acid-base interaction of stronger Lewis bases with silica shows a correlation between basicity and "complex" formation enthalpy [3].

Thus, the β-values for silica discussed in ref. [6] are useless.

HBD-properties (α-parameter)

We calculated the acceptor number of dried aerosil to AN = 49.1 and the value of the α-parameter for dried aerosil to $\alpha = 1.41$ [7]. These values are based on measurements utilizing $Fe(phen)_2(CN)_2$ and Michlers Ketone as probes. Dutta reported an α-value for silanol groups of dealuminated faujasite of $\alpha = 1.14$ [24] using salicylideneaniline (4) as probe. These α-parameters were determined by means of the peak-to-peak ratio R of the intensities of the absorption bands at 420 and 320 nm of the adsorbed probe dye 4 using the reflectance technique. Mathematical data processing was done according to Eq. 3 (taken from ref. [24]).

$$R(\varepsilon_{420\,nm}/\varepsilon_{320\,nm}) = 0.47\alpha - 0.44; \quad r = 0.998\ . \tag{3}$$

Measurements of the probe dye 4 in suspensions of aerosil in 1,2-dichloroethane yield α-values of 1.37 and 1.31 for dried and nondried aerosil, respectively. The concentration of the dye 4 was 0.4 mg per 300 mg aerosil in 20 ml 1,2-dichloroethane. Higher concentrations of 4 at the surface are not sensible due to the high absorption coefficient of the compound in the region of the 320 nm absorption band. For dried KG 60 we obtained an α-value of 1.13 in 1,2-dichloroethane which is very close to the α-value reported in ref. [24]. After adsorption of 4 on nondried KG 60 no absorption band could be detected about 400 nm. This result is unexpected.

The independently determined value of the α-parameter by the dye 4 for dried aerosil ($\alpha = 1.37$) supports our first reported value with $\alpha = 1.41$. In cyclohexane we obtained a value for the acidity of aerosil of $\alpha = 1.52$ by means of probe dye 4. Addition of triethylamine to 4 adsorbed on aerosil and suspended in 1,2-dichloroethane or cyclohexane leads to a decrease of the adsorption intensity of the adsorption band at 420 nm. Increasing the concentration of the amine component leads also to an increase in the 320 nm absorption band (see ref. [24]) because amine interacts with the phenolic OH-group of the probe dye too.

Dipolarity/polarizability (π^*-parameter)

We determined the dipolarity/polarizability value $\pi^* = 0.5$ for dried aerosil in 1,2-dichloroethane [7a]. Our value of that parameter is lower than all other values of π^*-parameters for silica and zeolithes reported in the literature up to now [6, 25]. Effenberger reported on a new dye 5 exhibiting a positive solvatochromism whose spectral shift depends only on the dipolarizability π^* [26] (Eq. (4)).

$$\nu_{\max}(5) = 21126\,\mathrm{cm}^{-1} - 3337\,\mathrm{cm}^{-1}(\pi^* - 0.1\delta) \qquad (4)$$

δ is a correction term for the polarizability of the solvent: $\delta = 0$ for aliphatics, $\delta = 0.5$ for halocarbons and $\delta = 1$ for aromatic solvents [10]. According to [7a] we measured the probe dye 5 dissolved in 1,2-dichloroethane and in the presence of aerosil. We found that the 5 was never adsorbed on aerosil or silica from a solution of 1,2-dichloroethane: the intensity of the π-π^*-transition of the dye at 18 000 cm^{-1} in 1,2-dichloroethane ($\pi^* = 0.82$) did not decrease and no trace of a new absorption could be detected in the region of 400 nm to 800 nm. This supports indirectly our value of the π^*-parameter of 0.5 (< 0.82) because, 1,2-dichloroethane ($\pi^* = 0.82$) undergoes stronger Van-der-Waals interactions with 5 than aerosil. In order to obtain a direct evidence for the accuracy of the π^*-value, we measured aerosil in cyclohexane ($\pi^* = 0$) as suspending liquid. In cyclohexane as suspending liquid dye 5 is adsorbed at the aerosil surface and a new absorption band appears at 640 nm. By using this value in Eq. (4) the value of the dipolarity/polarizability of the surface was determined, $\pi^* = 1.5$ for aerosil. The UV/VIS-spectra of several aerosil samples with the dye 5 are shown in Fig. 3. However, the differences between the results obtained in two different solvents raise two fundamental questions:

I) Does the suspending liquid influence the polarity of a surface or more accurately of the interface?

II) Does the spectral shift of the dye 5 reflect exclusively dipolarity and polarizability among other possible interactions?

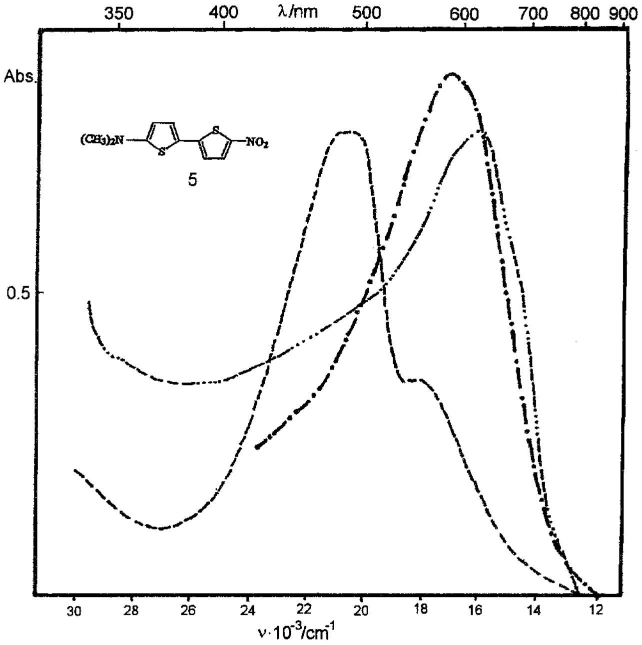


Fig. 3 UV/VIS-transmission spectra of 5-dimethylamino-5′-nitro-2,2-bithiophene adsorbed at aerosil, measured in cyclohexane ——— ··· ——— 5 measured in a suspension of cyclohexane, ---- after addition of triethylamine (20 mg/g aerosil), -·-·-·-·- 5 measured in 2,2,2-trifluoroethanol

Table 1 UV/VIS-absorption bands of the 5-N,N-dimethylamino-5′-nitro-2,2′-dithiophene dye measured in various halogenated and acidic solvents and in aerosil/cyclohexane suspension at 293 K. The α- and π^*-values of the solvents are taken from ref. [10]

Solvent	α	π^*	$\nu_{\max}(5)\ 10^{-3}/\mathrm{cm}^{-1}$
Cyclohexane	0.00	0.00	21.18
1,1,1-Trichloroethane	0.00	0.49	19.44
1,1,2-Trichlorethane	0.00		18.64
1,1-Dichloroethane	0.10	0.48	19.09
1,2-Dichloroethane	0.00	0.81	18.64
1,1,2,2-Tetrachloroethane	0.00	0.95	18.24
2,2,2-Trichloroethanol	–	–	17.88
2,2,2-Trifluoroethanol	1.51	0.73	17.24
1,1,1,3,3,3-Hexafluoro-2-propanol[a)]	1.96	0.65	16.28 (15.3 sh)
aerosil (nondried)/ cyclohexane	–	–	16.76
aerosil (dried at 150 °C)/ cyclohexane	–	–	16.16
aerosil/1,2-dichloroethane	–	–	18.64[b)]

[a)] The absorbance of the dye 5 disappeared after 15 min.
[b)] Only the absorbance of the dye 5 in 1,2-dichloroethane is obtained.

The results of UV/VIS-measurements of dye 5 are compiled in Table 1 for several other solvents showing high acidity (α) as well as dipolarity/polarizability (π^*). Protic solvents possessing a high value of $\alpha > 1.2$ obviously cause an additional bathochromic shift of the π-π^*-absorption of dye 5, independent of the value of the π^*-parameter. This effect is not attributed to the polarizability as shown by other halogen containing solvents (Table 1). However, the unusual bathochromic shift in acidic solvents suggests a specific acid base interaction similar to that of other dyes bearing nitro groups. By adding a strong basic compound, e.g., pyridine ($\beta = 0.64, \pi^* = 0.8$) or triethylamine ($\beta = 0.71, \pi^* = 0$) to the probe dye 5 being adsorbed on aerosil and suspended in cyclohexane a hypsochromic shift of the absorption band of the probe dye was observed. Unfortunately the dye desorbs from the

Table 2 Relevant values of parameters (E_T (30), AN, DN, α, β and π^*) for silica in 1,2-dichloroethane and comparison with common solvents. The values for the solvents are taken from ref. [8b]

Solvent	Solvent parameters							
	E_T(30/kcalmol^{-1}		AN		DN	π^*	α	β
Aerosil 300 (dried)	57.5[a]	58.5[b]	49.1[c]	50.3[d]	6 ± 1	0.5[a]	1.41[e]	0.06
Aerosil 300 (nondried)	59.0[a]	60.0[b]	53.2[c]	54.7[d]	12 ± 1	0.7[f]	1.35	0.27
KG 60 (dried)	57.6		47.8[d]		–	[g]	[g]	–
KG 60 (nondried)	59.0		52.2[d]		–	[g]	[g]	–
Water	63.1		54.8		18	1.09	1.17	0.47
2,2,2-Trifluoroethanol	59.8		53.3		–	0.73	1.51	–
Nitrobenzene	42.0		14.8		8.8	1.01	0.00	0.39
1,2-Dichloroethane	41.3		16.7		2.7	0.81	0.00	0.00
Cyclohexane	30.9		0.0		0.0	0.00	0.00	0.00

[a] The dye 6a is measured immediately after adsorption on the aerosil surface.
[b] After 2h the dye 6a is measured on the aerosil surface again. Since then the E_T(30)-value remains constant.
[c] Values are taken from ref. [7c].
[d] Corrected AN-values according to Eq. (1) from ref. [7b].
[e] Values are taken from ref. [7b].
[f] Calculated via Eq. (7) taking into account the values for nondried aerosil from this table.
[g] See text.

surface. This result shows that the adsorption and the sorptiochromism of dye 5 at aerosil is unfortunately accompanied by specific acid base interactions, too. The same result is obtained for KG 60 as silica sample. Thus, the dye 5 is not suitable as a probe for determination of the dipolarity and polarizability of acidic surfaces.

The absorption maximum of the charge-transfer band ($\nu_{\max,\mathrm{ct}}$) of the electron-donor-acceptor (EDA) complex of 3 with tetracyanoethylene (TCNE) is solvent dependent [21]. The $\nu_{\max,\mathrm{ct-value}}$ correlates with dipolarity/polarizability and basicity of the solvent as outlined in Eq. (5) [21]:

$$\nu_{\max,\mathrm{ct}}\,10^{-3}/\mathrm{cm}^{-1} = 3.05\,\beta - 2.51\,\pi^* + 16.73 \tag{5}$$

$$r = 0.963, \quad n = 20, \quad s = 0.052\,.$$

The 3/TCNE-complex is completely adsorbed from 1,2-dichloroethane at the aerosil surface. The shift of the CT-band from 14,880 cm^{-1} to 15,300 cm^{-1} corresponds to a dipolarity/polarizability value of $\pi^* = 0.6$ (using a β-value of 0.06 by putting the values into Eq. (5)) for aerosil. This result also supports our value for the π^* parameter of aerosil from ref [7a]. The 3/TCNE complex is also adsorbed at KG 60, however, rapid side reactions take place at dried KG 60 which disturb the correct determination of $\nu_{\max,\mathrm{ct}}$. Nevertheless, the π^*-value for nondried KG 60 with $\pi^* = 0.77$ ($\nu_{\max,\mathrm{ct}} = 15\,600$ cm^{-1} of the adsorbed complex 3/TCNE) can be obtained in a similar way.

E_T(30)-parameter

The E_T(30)-solvent-parameter is defined as the molar transition energy of the intramolecular CT-absorption of the dye 6a according to Eq. (6) [8]. Marcus [27] reported that the E_T(30)-parameter can be expressed by a multiparameter approach considering the Kamlet–Taft solvent parameters α, β, and π^* (Eq. (7)).

$$E_T(30)/\mathrm{kcalmol}^{-1} = \nu_{\max}(6a)\,2.8591\,[\mathrm{cm}^{-1}] \tag{6}$$

$$E_T(30) = 12.99\,(\pi^* - 0.21\delta) + 14.45\alpha + 2.13\beta + 30.2 \tag{7}$$

$$r = 0.987, \quad n = 100\,.$$

The E_T(30)-parameters for aerosil and KG 60 are determined by measuring the UV/VIS-absorption band of dye 6a adsorbed on silica suspended in 1,2-dichloroethane (see Table 2). Table 2 summarizes all "solvent"-parameters for aerosil suspended in 1,2-dichloroethane and KG 60 suspended in 1,2-dichloroethane which have been measured and calculated by us. The E_T(30)-parameter values agree excellently with data given by Drago ref. [4].

According to Eq. (7) the values of the α-, π^*- and β-parameter of dry aerosil from Table 2 are confirmed finally by the value of the E_T(30)-parameter obtained for aerosil.

With $\delta = 0$ (δ means correction term for the polarizability which should be zero for silica) the calculated E_T(30) value of aerosil approaches $E_T(30) = 57.2$. The measured E_T(30)-parameter of dried aerosil in 1,2-dichloroethane is

$E_T(30) = 57.5$. The excellent agreement between those independently obtained $E_T(30)$-parameters should be an evidence that the solvatochromism of all five indicators (1^+, 2, 3, 4, 6a) adequately reflect the overall surface properties of silica. Therefore, our values of the α-, π^*- and ß- parameters for silica are reliable constants using 1,2-dichloroethane as suspending agent. The higher polarity of nondried aerosil is caused by the dipolarity of the water layer on the surface. The same explanation should be valid for the overall polarity of dried and nondried KG 60. The separate determination of the α- and π^*-value for dried and nondried KG 60 seems to be more problematic than for aerosil. We believe that the pore size distribution of KG 60, which is changed after adsorption of indicators (becomes smaller), is responsible for the fact that the indicators used lead to different values for the acidity and dipolarity/polarizability of dried and nondried KG 60. Therefore, we recommend the application of the single well defined $E_T(30)$-parameter or the AN-parameter for KG 60 in correlation analysis (from Table 2).

To prove the applicability of the $E_T(30)$-solvent polarity scale for the determination of solvent polarity values of silica, e.g., aerosil/1,2-dichloroethane suspension, we carried out titrations of the dye 6a adsorbed on aerosil with triethylamine as base. A characteristic spectra series is shown in Fig. 4.

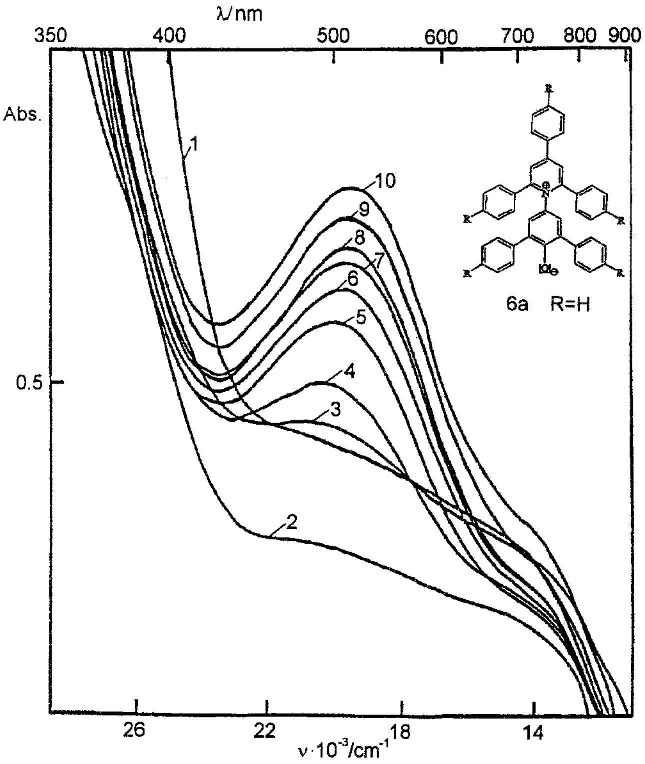


Fig. 4 UV/VIS-transmission spectra of the N-pyridinium-phenolate betaine dye 6a adsorbed at nondried aerosil; measured in dependence of the triethylamine concentration added in 1,2-dichloroethane; 1 = without triethylamine, 2 = 7.3 mg/g, 3 = 14.5 mg/g, 4 = 21.8 mg/g, 5 = 29.0 mg/g, 6 = 36.3 mg/g, 7 = 43.5 mg/g, 8 = 50.8 mg/g, 9 = 58.0 mg/g and 10 = 65.3 mg/g

From Fig. 4 two different effects can be observed:

I) Increasing triethylamine concentrations leads to an increase in the absorption intensity of 6a. A possible explanation is that the phenolate oxygen (from 6a) reacts with active protons of the silica surface deriving from surface sites possessing silanol groups with pK_A-values less than 7. The protonated form of 6a is colorless [28]. Therefore a stronger base than 6a (e.g. triethylamine) will capture the active protons of the surface (see Scheme 4).

II) There is a bathochromic shift of the dye absorption band because the surface polarity of aerosil is a function of the amine concentration (see Fig. 5). The surface acidity of silica decreases by increasing the amine concentration on the surface.

Figure 5 shows that the silica surface possesses two different adsorption sites (the differently marked lines indicate the limits). The energy differences of the two different adsorption sites or polarity levels concerning the $E_T(30)$ polarity scale for dried and nondried aerosil as function of the triethylamine concentration agree amazingly well with results obtained by calorimetric measurements reported by Drago [4] for the titration of silica with pyridine in cyclohexane (Table 3).

These results show that the surface polarity of nondried silica is distributed over a wider range than that of dried aerosil. Unfortunately, the dye 6a is insoluble in cyclohexane, therefore our results cannot be compared directly with Drago's [4] calorimetric results obtained in cyclohexane. Thus we used the tertiary butyl substituted dye 6b which is soluble in both solvents, i.e., 1,2-dichloroethane and cyclohexane. 6b yields an $E_T(30)$-value for dried aerosil in cyclohexane of $E_T(30) = 57.6$ ($\nu_{max} = 19\,650\ \mathrm{cm}^{-1}$). The agreement among both dyes was expected due to their linear correlation with each other [8]. Despite the good agreement among the determined values of the polarity parameters obtained with both dyes the following results concerning the applicability of 6b as surface indicator should be briefly completed. The tertiary butyl group bearing dye 6b is adsorbed very weakly on nondried aerosil. Therefore no sharp maximum can be detected. In the case of dried aerosil, the dye 6b is adsorbed very well. This shows that a water layer on the surface prevents the interaction of the lipophilic tertiary butyl groups with the siloxane bridges on the silica surface. Siloxane bridges undergo dispersion interaction with the tertiary butyl groups of 6b as reported in ref. [3] for similar combinations.

Scheme 4 Possible side reaction of 6a with protones of the silica surface

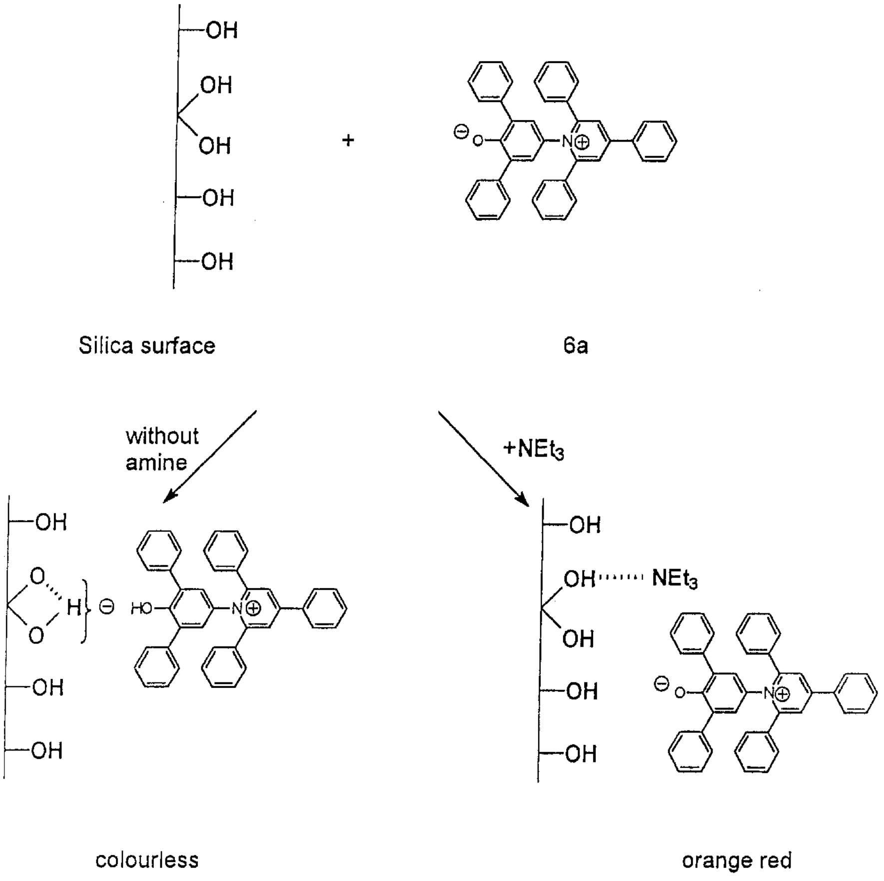


Fig. 5 Dependence of the surface polarity $E_T(30)$ of dried (○) and nondried (●) aerosil on the triethylamine concentration measured in 1,2-dichloroethane at 293 K

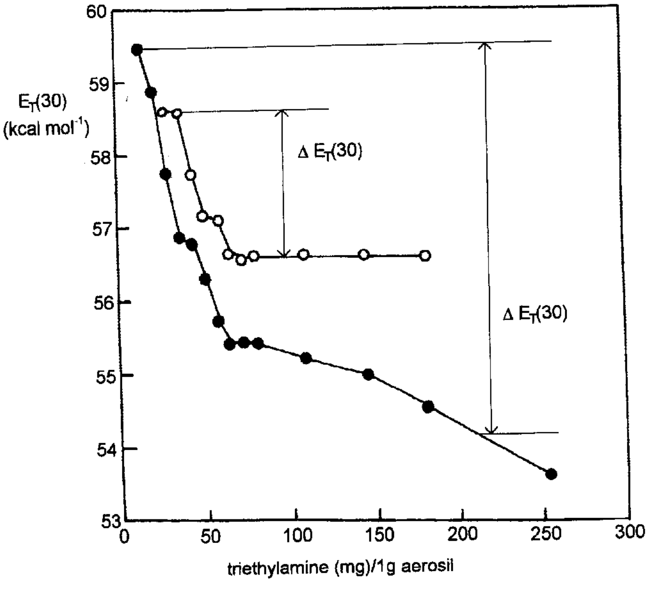


Table 3 Comparison of the energy differences (in kcal mol^{-1}) of the polarity-acidity state levels of dried and nondried silica obtained by solvatochromic measurements (this paper) and calorimetric titration (from ref. [4], Table 1)

Difference of interaction enthalpy	Dried silica	Nondried silica	Acid-base combination
$E_T(30)(1) - E_T(30)(2)$	2.1	5.5 ± 1	aerosil/triethylamine in 1,2-dichloroethane
$\Delta_r H(1) - \Delta_r H(2)$	2.3	7.3	silica gel/pyridine in cyclohexane

It is obvious that different substituted dyes and different modified silicas can be used as models to study intermolecular forces between colloid particles [29]. That the interaction of solvents with silica and alumina can be described by linear solvation relationships (considering the Kamlet–Taft-parameters) is also demonstrated for the solute adsorption energy [30].

Conclusion

The solvatochromism comparison concept of Kamlet and Taft [10] for the determination of α-parameters is not suitable for acidic surfaces. Taking the difference of the spectral shift of 4-nitroanisole (from ref. [6]) and of Reichardt's dye into account a negative α-parameter is obtained. We are afraid that nitrosubstituted aromatic compounds are not convenient as dipolarity indicators for acidic surfaces, colloids, and polymers. It could be demonstrated that the five probe dyes Cu(tmen) (acac) $^+ClO_4^-/B(C_6H_5)_4^-$, $Fe(phen)_2(CN)_2$, Michlers Ketone, salicylideneaniline and Reichardt's Betaine are excellent solvatochromic indicators for the determination of values of surface polarity parameters for silica. All five indicators can be used independently from each other due to their precisely characterized solvatochromism. The "solvent" parameters for aerosil-silica compiled in Table 2 show silica as an excellent medium for electrophilic organic reactions. Silica has a high polarity and acceptor strength accompanied with a very low donor strength. Liquid water possessing similar values of polarity like silica, but a higher value of the basicity parameters, reacts with carbenium ions in solution. In contrast, the reaction of carbenium ions with water on the surface of silica occurs much slower. For that reason the silica surface is an excellent "solvent" for carbenium ion chemistry.

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