Analysis of the Polarity of Silica Surfaces as Reaction Media. Behavior of Adsorbed Solvatochromic Indicators

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The Kamlet–Taft solvatochromic indicator method, applied to the analysis of the polar properties of silica surfaces, suggests that dipolarity/polarizability (π^*) is the most important contributor to the polar properties of the surface, followed by hydrogen bond donation (α). There is considerable dispersion of the π^*_i values of individual π^* indicators and of the β_i values of individual β indicators. The greater dispersion means that interactions with silica are more specific for the structure of the adsorbate than are interactions between a liquid solvent and its solute. The dispersion of the π^*_i and β_i values may be due in part to the existence of more than one kind of adsorption site on the silica surfaces.[1] The dependence of the solvatochromic parameters on the monolayer fraction also confirms the previously observed existence of more than one type of adsorption site.

A number of unique products, unusual product ratios, unusually high rates, and various features of mechanistic interest, have been noted when reactions are carried out on the surface of amorphous silica.[1-8] In some cases polar reactions carried out in this environment have rates many orders of magnitude greater than those in ordinary liquid solution.[2,3,8] For example, in ordinary solvents benzoyl peroxide decomposes exclusively by the homolytic route. The rates are moderate at 80 °C and negligible at room temperature. On silica at room temperature the decomposition reaction is primarily heterolytic and its rate is many orders of magnitude greater than that of the reaction in solution extrapolated to the same temperature.[8]

The silica surface in these reactions is clearly an extraordinarily "polar" medium, but the precise nature of its "polarity" was not immediately apparent. One way of adding precision to the concept of polarity is the analysis of medium effects using shifts in the absorption maxima of solvatochromic indicators, a method that has been widely applied to liquid solvents.[9-13] In this paper we describe the behavior of several such indicators adsorbed on silica and draw some conclusions about the nature of the interactions between the surface and adsorbed reagents.

Analysis of a medium effect usually requires a model with several solvent–solute interaction mechanisms. The surface functional groups on silica, for example, might affect an adsorbed reagent not only by dipole or induced dipole interaction mechanisms but also as the donors or acceptors of the proton in hydrogen bonds. The Kamlet–Taft solvatochromic comparison method uses the pattern of frequency shifts of solvatochromic indicators to assign values for parameters α and β, representing the

ability of the solvent to act as the hydrogen bond proton donor or acceptor, and π^*, representing dipolarity and/or polarizability. These parameters are used in linear free energy equations like (1) to correlate log k or other sol-

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta + ... \qquad (1)$$

vent-dependent quantities (XYZ). Although hydrogen bonding and dipolarity/polarizability cannot really be completely independent as assumed in eq 1, the approximation has proved useful for liquid solvents, and there have been many successful applications.

Kamlet and Taft based the solvent-polarity/polarizability scale represented by the parameter π^* on the average behavior of a set of π^*_i indicators in a set of solvents. Initially the combinations of indicator and solvent were chosen to minimize perturbations by other interactions such as hydrogen bonding. Thus the indicators used to establish the scale were not hydrogen-bond donors, although they might function as hydrogen-bond acceptors. Also, the solvents used in establishing the scale were unable or unlikely to act as hydrogen-bond donors.[9,10] An individual π^* value, π^*_i, for any single one of these indicators in a given solvent can be obtained by solving the corresponding regression equation (2).

$$\nu_{i,max} = \nu_{i,0} + s_i\pi^*_i \qquad (2)$$

In hydroxylic solvents the polarity/polarizability interpretation of the solvatochromic frequency shifts is obscured by interference from hydrogen bonding. However, Kamlet and Taft have adduced reasons for believing that indicators 1–4 of Table I suffer minimally from this interference.[9,10] The individual π^*_i values calculated for this restricted set of indicators are generally within a few percent of their mean values, and the latter have been proposed, with some reservations, as π^* values for a number of hydroxylic solvents. Some examples are 0.41 for 2-methyl-2-propanol, 1.09 for water, 0.92 for ethylene glycol, 0.71 for 2-methoxyethanol, 0.66 for acetic acid, and 0.73 for trifluoroethanol.[13]

The data for silica and the four indicators preferred for hydroxylic solvents,[9] 4-nitroanisole (1), *N,N*-diethyl-3-nitroaniline (2), 4-methoxy-β-nitrostyrene (3), and 1-ethyl-4-nitrobenzene (4), are given in Table I.

The behavior of these indicators on silica differs from their behavior in any solvent in two important ways: not only is the mean of the four π^*_i values more than twice the value found for any liquid but also the variation in π^*_i is much greater. For P_1 silica the grand mean π^* is 2.30. The mean π^*_i values on the same silica range from 0.81 for **2** to 4.00 for **4**. The absorption peaks are reasonably sharp

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Table I

ind.[d]	P₁ silica[a]			P₀ silica[a]		
	wt %[b]	$\nu_{max}{}^{c}$	π^*	wt %[b]	$\nu_{max}{}^{c}$	π^*
1	0.28	28.42	2.39	0.26	28.18	2.49
	0.50	27.92	2.59	0.54	27.49	2.77
	6.20	27.35	2.83			
	10.08	27.15	2.91			
		mean π^* =	2.68		mean π^* =	2.63
2	0.24	23.67	0.86	0.29	24.05	0.69
	0.53	23.99	0.71	0.50	23.61	0.89
	6.04	23.69	0.85			
		mean π^* =	0.81		mean π^* =	0.79
3	0.26	26.26	1.61	0.29	26.27	1.60
	0.51	26.25	1.61	0.50	25.64	1.87
	6.02	25.60	1.89			
		mean π^* =	1.70		mean π^* =	1.74
4	0.29	29.32	3.70	0.31	27.69	4.42
	0.50	29.41	3.66	0.58	28.49	4.06
	6.05	28.11	4.23			
	10.24	27.69	4.42			
		mean π^* =	4.00		mean π^* =	4.24
5	0.25	23.34	1.31	0.26	23.36	1.31
	0.51	23.92	1.13	0.56	23.30	1.33
	6.00	23.87	1.15			
		mean π^* =	1.20		mean π^* =	1.32
6	0.29	26.33	2.03	0.27	26.41	1.99
	0.51	26.02	2.18	0.53	25.76	2.31
	6.05	25.52	2.43			
		mean $^*\pi$ =	2.21		mean π^* =	2.15

[a] Silicas P₁ and P₀ correspond to silicas P₁H₁ and P₀H₁ of ref 1. [b] Load is the wt % of the indicator. For these indicators a load of 0.25% is calculated to occupy (average) about 0.7% of the N₂ area of the surface, but probably a considerably higher proportion of the area accessible to molecules of the size of the indicators. [c] The frequency (kKaysers) in this column is that which which divides the area between the absorption curve and the line drawn at ¹/₂ the maximum absorption into equal parts. This frequency is usually close to that at the apparent maximum, but is less subjective. It should also give a better representation to the populations of nonequivalent adsorption sites, which might differ in their absorption frequencies. [d] Indicators, their ν_0 and s values: (1) 4-nitroanisole,[10] 34.17, 2.410; (2) N,N-diethyl-3-nitroaniline,[10] 25.57, 2.212; (3) 4-methoxy-β-nitrostyrene,[10] 30.00, 2.329; (4) 1-ethyl-4-nitrobenzene,[9] 37.67, 2.259; (5) N,N-diethyl-4-nitroaniline,[10] 27.52, 3.182; (6) 4-(dimethylamino)benzophenone,[10] 30.41, 2.013.

and the π^*_i values do not depend appreciably on the method used to locate the maximum. The same pattern and nearly the same π^*_i values are obtained from independent experiments on P₀ silica, a slightly less pure grade from the same source. All four indicators give absorption maxima in hexane and in ethanol in good agreement with the values in the literature. The very large differences between the behavior of the indicators on silica and in any liquid solvent are therefore real.

Apparently dipolarity/polarizability is an important component of the "polarity" of silica but is much more dependent on the specific structure of the adsorbate. In view of this structural specificity, it may be necessary to develop rules for hand-picking indicators appropriate for use with a given reaction if the solvatochromic comparison method is ever to be used for predicting rates or other XYZ quantities on silica.

One contributor to the greater dispersion of the π^*_i on silica could be the known heterogeneity of the adsorption sites.[1] If the indicators differ in selectivity for the several types of adsorption site, then each indicator is reporting on a different environment. If this is the explanation, the individual π^*_i values should depend on the monolayer fraction. At low monolayer fractions an indicator adsorbed preferentially on sites of one type would be forced, at higher monolayer fractions, to begin to lodge elsewhere. In fact (Table I), there is a tendency for the individual π^*_i values to change as the monolayer fraction is increased, but the change is very small compared to the differences

in the values for different indicators.

Another possible explanation is that the hydrogen bond donating (HBD) or accepting properties (HBA) of the medium interfere more with the measurement of π^*_i on silica than they do in solution and that *these* are specific for each indicator. The parameters α and β, which are measures of these properties, are discussed in the next section. Unlike the π^*_i values, however, they are within the range seen for ordinary solvents. Although they also change with increasing monolayer fraction, the change is moderate.

Finally, it is plausible that the interaction of the π^*_i indicators with the rigid constellations of dipoles (or polarizable groups) on the silica surface is inherently more specific for different adsorbate structures than is the interaction with the more mobile environment surrounding the indicator in solution. In this respect the interaction can be compared to the interaction of an adsorbed substrate with an enzyme.

The α and β Parameters. α. The absorption frequencies of two solvatochromic indicators, which differ in their ability to act as acceptors of hydrogen bonds, will be linearly related if the solvent series is restricted to non-hydrogen bond donating (non-HBD) solvents. One example is the pair consisting of Dimroth's betaine (7), a hydrogen bond accepting indicator, and 4-nitroanisole (1).[13] Points for *HBD Solvents* deviate from the non-HBD regression line, and the deviation is a measure of the hydrogen bond donating ability of the HBD solvent. The

Table II

	P₁ silica				P₀ silica			
wt %[b]	π^{*a}	α_1	β_1	β_{2a}	π^{*a}	α_1	β_1	β_{2a}
0.25	1.98	1.22	0.43	0.68	2.08	0.93	0.48	0.49
0.5	1.98	0.82	0.56	0.61	2.21	0.69	0.66	0.53
6	2.23	0.34	0.92	0.94				

[a] Mean of indicators 1–6. [b] Pooled data for approximately these wt % values.

parameter α_1 derived from the 7–1 pair is defined by eq 3 and 4.[13] The second term in (3) is the absorption frequency calculated from the regression line. The scaling

$$\Delta\Delta\nu(7-1) = \nu(7)_{max} - \nu(7)_{calcd} \qquad (3)$$

$$\alpha_1 = \Delta\Delta\nu(7-1)/6.24 \qquad (4)$$

factor 6.24 sets α equal to 1.00 for methanol. We were unable to use a second measure of α, based on Brooker's merocyanine[18] and 4-nitroanisole, because the merocyanine on silica proved to be unstable to light.

β_1 **and** β_2. The parameter β_1 is derived from the deviation of a hydrogen bond accepting solvent (HBA) from the regression line correlating the absorption maximum of the non-HBD indicator *N,N*-diethyl-4-nitroaniline (5) with that of the hydrogen bond donating indicator 4-nitroaniline (8). It is defined by eq 5,[12] in which the scaling factor 2.80 assigns the value 1.00 to the solvent hexamethylphosphoramide. The parameter β_2 is similarly defined by eq 6 and the absorption frequencies of 4-nitroanisole (1) and 4-nitrophenol (9).

$$\beta_1 = -\Delta\Delta\nu(8-5)/2.80 \qquad (5)$$

$$\beta_2 = -\Delta\Delta\nu(9-1)/[(2.80)(0.825)] \qquad (6)$$

The liquid media that might be expected to resemble silica surfaces most closely are amphiprotic solvents, and it is unfortunate that the behavior of solvatochromic indicators in such solvents is rather complex. Although $-\Delta\Delta\nu(9-1)$ is an excellent linear function of $-\Delta\Delta\nu(8-5)$ in solvents that are hydrogen bond acceptors but not hydrogen bond donors, points for alcohols fall on an entirely different line.[12] To make a β_2 value for amphiprotic solvents compatible with the β_1 scale, β_{2a} should be defined as in eq 7, which is derived from the special regression line for $-\Delta\Delta\nu(9-1)$ vs. $-\Delta\Delta\nu(8-5)$ found for alcohols.

$$\beta_{2a} = [-\Delta\Delta\nu(9-1) - (0.88)(0.406)]/[(0.406)(2.80)] \qquad (7)$$

As can be seen from Table II, β_1 and β_{2a} still do not agree very well, again suggesting that the interaction of the adsorbate with the silica is quite specific.

Both β_1 and β_{2a} increase with the monolayer fraction, while the hydrogen bond donor parameter α decreases. The sites progressively occupied at higher monolayer fractions have a greater ability to act as proton acceptors in H-bonding, accompanied by a lower ability to act as proton donors. At a given monolayer fraction, the H-bond donating abilities of P₀ silica appear to be *less* than those for P₁ silica. It is interesting to note[1] that the acid–base, or *proton transfer*, indicator, *p*-(dimethylamino)azobenzene is yellow on P₁ silica and red on P₀ silica. In water this indicator changes from red to yellow in the pH range 2.9–4.0.

The fact that the mean π^* value of the π^*_i indicators on the silica surfaces is greater than the largest values found for ordinary solvents suggests that polarity/polarizability is the most important contributor to the polarity of the surface. The next most important component is the hydrogen bond donating property, measured by α_1, which is comparable at low monolayer fractions to the highest values found for liquid solvents. The least important component is the hydrogen bond acceptor property, since β_1 and β_{2a}, except at high monolayer fractions, are within the lower part of the range for ordinary solvents. The dispersion of π^*_i and α_2 values, as well as their dependence on monolayer fraction, confirms the existence of more than one kind of adsorption site on silica.[1]

Experimental Section

The Indicators. *N,N*-**Diethyl-3-nitroaniline**[14] was prepared from 3-nitroaniline: ¹H NMR (270 MHz, CDCl₃) δ 1.2 (t, 6 H), 3.4 (q, 4 H), 6.9 (m, 1 H), 7.35 (m, 3 H); UV λ_{max} (hexane) 389.2 nm (lit.[9] 389.1 nm).

N,N-**Diethyl-4-nitroaniline** was prepared from diethylamine and 4-nitro-1-chlorobenzene: mp 76–77 °C (ethanol) (lit.[15] mp 77–78 °C); ¹H NMR (270 MHz, CDCl₃) δ 1.2 (t, 6 H), 3.45 (q, 4 H), 6.55 (d, 2 H), 8.08 (d, 2 H); UV λ_{max} (hexane) 359.5 nm (lit.[12] 360.8).

4-Methoxy-β-nitrostyrene was made from 4-methoxybenzaldehyde and nitromethane:[16] mp 86.5–88 °C (ethanol) (lit.[16] mp 86–87 °C); IR (CH₂Cl₂) 1618, 1520, 1360 cm⁻¹; UV λ_{max} (hexane) 331.5 nm (lit.[9] 331.3); ¹H NMR (270 MHz, CDCl₃) δ 3.82 (s, 3 H), 6.95 (d, 2 H), 7.45 (s, 1 H), 7.52 (d, 2 H), 7.95 (d, 1 H).

N-**Methyl-2-nitro-*p*-toluidine** was made from 2-nitro-*p*-toluidine and methyl iodide:[17] mp 84.5–86.0 °C (lit.[17] mp °C); 85–86 IR (CH₂Cl₂) 3395, 1540, 1368 cm⁻¹; ¹H NMR (270 MHz) δ 2.26 (s, 3 H), 3.05 (s, 3 H), 6.75 (d, 1 H), 7.3 (q, 1 H), 7.96 (s, 1 H); UV λ_{max} (hexane) 417.5 nm (lit.[9] 417.3).

Dimroth's betaine was made by the procedure of Dimroth et al.:[20] mp 220–271 °C (lit.[20] mp 205–276 °C); UV (ethanol) λ_{max} 552.5 nm (lit.[11] 551.3).

4-Nitroanisole from Aldrich Chem. Co. was recrystallized from ethanol: mp 52–53 °C (lit.[21] 54 °C); IR (CH₂Cl₂) 2950, 1515, 3155, 1198, 1054 cm⁻¹; ¹H NMR (270 MHz) δ 3.9 (s, 3 H), 6.94 (d, 2 H), 8.18 (d, 2 H); UV (hexane) λ_{max} 291.0 nm (lit.[12] 291.5).

4-Nitro-1-ethylbenzene from Aldrich Chem. Co.: IR (CH₂Cl₂) 2965, 2925, 2885, 1615, 1475, 1535, 1365 cm⁻¹; ¹H NMR (270 MHz) δ 1.3 (t, 3 H), 2.75 (q, 2 H), 7.35 (d, 2 H), 8.15 (d, 2 H); UV λ_{max} (hexane) 263.8 nm (lit.[9] 264.7).

4-Nitroaniline from Aldrich was recrystallized from benzene: mp 147–148 °C (lit.[21] mp 147.5 °C); IR 3399, 3495, 1650, 1545, 1375 cm⁻¹; UV λ_{max} (hexane) 318.6 nm (lit.[12] 319.5).

4-(Dimethylamino)benzophenone was recrystallized from ethanol: mp 90–91 °C (lit.[22] mp 92–93 °C); IR (CH₂Cl₂) 3050, 1655, 1605 cm⁻¹; ¹H NMR (270 MHz) δ 3.05 (s, 6 H), 6.65 (d, 2 H), 7.5 (m, 3 H), 7.7 (d, 2 H), 7.85 (d, 2 H); UV λ_{max} (hexane) 329.6 nm (lit.[9] 327.0).

4-Nitrophenol was recrystallized from ethanol: mp 112–113 °C (lit.[23] mp 114 °C); IR (KBr pellet) 3325, 1515, 1345, 880 cm⁻¹; ¹H NMR (270 MHz) δ 5.63 (s, 1 H, D₂O-exchangeable) 6.88 (d, 2 H), 8.15 (d, 2 H); UV λ_{max} (hexane) 284.0 nm (lit.[12] 285.1).

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P₁ and P₀ Silicas. These were of the same grade and from the same supplier as the silicas called P_1H_1 and P_0H_1 in ref 1. Before use they were heated at 125 °C for 3–4 days and allowed to cool in a vacuum desiccator.

Adsorption of Indicators. The slurry evaporation method[1] was used. The indicator was applied in ether dried over 4-Å molecular sieves, except for 4-nitroaniline and 4-nitrophenol, which were applied with dry acetone. After removal of solvent on a rotary evaporator, the container was connected to a vacuum pump and pumped for 6 to 12 h to remove any remaining solvent.

The Reflectance Spectra. The instrument was a Cary Model 14 spectrophotometer equipped with an integrating sphere. The integrating sphere was freshly coated with successive layers of white primer, several water-soluble top coats, 15 sprayed coats

of $BaSO_4$ suspended in water, and finally with 10 coats of MgO from a burning Mg ribbon.[24]

The silica samples with the adsorbed indicator were poured onto microscope slides previously sprayed with a clear polyurethane and allowed to dry for 4–5 min. The sample port of the integrating sphere was covered with clear plastic wrap to keep any loose silica from contaminating the sphere. The sample slide then was placed over the port and clamped in place with a block of $MgCO_3$. Another block of $MgCO_3$ was placed over the reference port. Each spectrum was scanned 3 times.

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Structures of the Ratibidanolides, Sesquiterpene Lactones with a New Carbon Skeleton, and Unusual Xanthanolides from *Ratibida columnifera*[1]

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Structures and stereochemistry of two sesquiterpene lactones from *Ratibida columnifera* which possess a new rearranged eudesmane derived carbon skeleton were deduced by NMR spectroscopy and X-ray diffraction. The main lactone fraction of this plant consisted of a family of unusual xanthanolides whose structures were established in the same manner. Other constituents included the new nerolidol derivative (3S*,5R*)-(−)-5-hydroxy-9-oxonerolidol.

The eudesmane cation A and its epimers, or their biological equivalents, have been invoked[2–4] as progenitors of the eremophilane and spirovetivane classes of sequiterpenes, angular methyl migration (path a) leading to the eremophilanes and nootkatanes (B), and ring contraction of the six-membered ring bearing the isopropyl substituent leading to the hinesanes, solavetivanes, and agarospiranes (C). We now describe two representatives **1** and **5** of the previously unknown carbon skeleton D which results from the third possible rearrangement mode of A, namely ring contraction of the six-membered ring bearing the methyl substituent (path c). Lactones **1** and **5** were isolated from the common prairie coneflower *Ratibida columnifera* (Nutt.) Woot. & Standl.[5] together with isolantolactone (**8**), the elemadienolide **9**, a family of unusual xantholides **10a–f, 11, 12a,b,** and **14a–d**, the new nerol derivative **15a**, the thiophene acetylenes **17**[7] and **18**[7] and the flavone hispidulin (**19**).[8,9]

We discuss first the structure elucidation of **1** and **5**, members of the new class of ratibidanolides, which are based on what we propose to name the ratibidane carbon
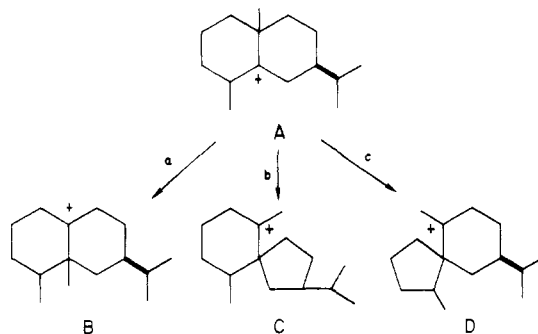
skeleton. That the two compounds were α-methylene-α,β-unsaturated-γ-lactones and double bond isomers, with **1** possessing partial structure E (numbering as in final formula) and **5** the corresponding structure with an endocyclic double bond between C-9 and C-10, was clear from inspection of the ¹H NMR spectra (Table I) and spin decoupling experiments. By irradiating at the frequencies of the typical narrowly split doublets of H-13a,b near δ 6.25 and 5.65 the signal of H-7 was located at δ 3.04; this signal was split so as to indicate the presence of three vicinal protons. Two of these, H-6a and H-6b, constituted the AB part of an ABX system and hence represented two protons next to a quarternary center. The third, H-8 near δ 4.6 and hence the proton under the lactone oxygen, was in the case of **1** additionally coupled to two mutually coupled protons (H-9a,b) whose chemical shift indicated that they were allylic to a nonconjugated =CH₂ group made evident by the ¹H and ¹³C NMR spectra (Table II). In the case of **5**, H-8 was additionally coupled to a vinylic proton which in turn was allylically coupled to the protons of a vinylic methyl group. Reaction of the α-methylene-α,β-unsaturated-γ-lactone function of **1** with diazomethane to give pyrazoline **2** and with 4-bromothiophenol to give adduct **3** produced the expected spectral changes as did ep-

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