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Getting a Library of Activities from a Single Compound: Tunability and Very Large Shifts in Acidity Constants Induced by Sol−Gel Entrapped Micelles

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Abstract: Acidity constants (in terms of K_i values) can be fine-tuned, their values can be pushed to extremes, and their location can be placed either at the basic or acidic range of the pH scale, by tailoring intra-cage properties of SiO_2 sol−gel materials with surfactants. With the entrapped "solid-state pseudomicelles", an 8-orders magnitude K_i shift—from the high-basic pH region to the acidic one—was obtained for acid fuchsin (AF); and tunability of the pK_i values of the solvatochromic dye $E_T(30)$ and of crystal violet over much of the pH scale was achieved. This tailoring of various activities from the same dopant was achieved either by utilizing surfactants of different nature or by utilizing mixtures of anionic/cationic surfactants. The extraction of a wide range of reactivities from a single compound and the ability to fine-tune it is a powerful concept with potential extensions beyond acid/base reactions.

Introduction

We have reported recently in this journal[1] that sol−gel entrapped cetyltrimethylammoniumbromide (CTAB) at low, sub-templating concentrations[2] was found to affect the chemical and spectral properties of codoped pH indicators. Whereas the original aim of the field of doped sol−gel materials has been mainly to transfer a known solution reaction to the ceramic sol−gel environment while preserving its characteristic features[3,4] (as reflected, for instance, in the voluminous activity in the field of sol−gel pH sensors[3a,4a]), the observation with the entrapped pseudomicellar CTAB[1,5] has pointed to a possibility of greatly extending that original aim. Thus, taking into account the ability of surfactants to alter the performance of indicators in solution[6−9] and taking into account the accumulated know-how on the behavior of molecules solubilized within micelles/solid materials systems[10] have led to the hypothesis that entrapment of *different* surfactants, may have the potential of opening a *library of reactivities from a single, specific dopant*.

Indeed, we report here that the preliminary observation with CTAB[1] turned out to be only the tip of an iceberg: the scope of the methodology has been found to be wide, and its potential, powerful. We show here that by careful selection of sol−gel entrapped surfactants, changes in activity of dopants can be induced, from colossal magnitudes down to delicate fine-tuning. The method is convenient and general: Rather than changing molecular performance by tedious synthetic methods, affecting such changes through control of the environment of the reacting molecule is, in principle, simpler, and to this is added the convenience of an "off-the-shelf" solid micellar system. The combination of two caging environments which are known to affect molecular properties—sol−gel entrapment[11] and micellar caging[8]—provide the desired rich library of interactions to be

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utilized at various relative weights: ionic interactions of various types, hydrogen bonds, hydrophobic interactions, and tight ion-pairing.

Abbreviations Used in this Report. The indicators: AF: acid fuchsin; CV: crystal violet; $E_T(30)$: 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)-phenolate. The surfactants: CPB: cetylpyridinium bromide; CTAB: cetyltrimethylammonium bromide; CTAC: cetyltrimethylammonium chloride; CTApTS: cetyltrimethylammonium *p*-toluenesulfonate; SB-16: palmityl sulfobetaine; SDS: sodium 1-dodecanesulfonate; TX-100: Triton X-100. Sol−gel precursor: TMOS: $Si(OCH_3)_4$.

Experimental Details

Chemicals. The indicators, crystal violet, acid fuchsin, and $E_T(30)$ were from Aldrich. TMOS was from Aldrich. The surfactants: CPB (Aldrich, cationic), CTAB (Aldrich, cationic), CTAC (Aldrich, cationic), CTApTS (Sigma, cationic), SB-16 (Sigma, zwitterionic), SDS (BDH, anionic), TX-100 (BDH, nonionic).

Entrapment Procedure. For entrapment, methanol (2.5 mL for CV and AF; 1.5 mL for $E_T(30)$), 2.5 mL of TMOS and 1.0 mL of an 8.2×10^{-2} M methanolic surfactant solution, for example, CTAB (molar ratio, CTAB: silane $= 4.8 \times 10^{-3}$) were premixed and sonicated for 5 min. Then water (2.3 mL for CV and AF; 2.4 mL for $E_T(30)$) and 0.1 mL of a 0.1% (by weight) aqueous solution of the indicator (or 0.5 mL of a 1.0% methanolic solution for $E_T(30)$) were added to the organic phase, and the final mixture was sonicated for an additional 10 min. (Final water:silane molar ratio = 7.6, and ratios of indicator:surfactant for the different surfactants were 2.1×10^{-3} for AF, 3.0×10^{-3} for CV, and 8.7×10^{-2} for $E_T(30)$). After the sonication, the mixture was poured into a Petri dish, covered, and left at room temperature for 5 days for gelation and initial shrinkage. The wet gel was then dried for 2 days in an oven at 45−50 °C, during which the gel shrank further, resulting in a transparent disk with typical dimensions of 26 mm in diameter and 2.5 mm in thickness. The $E_T(30)$/CTAC:SDS/SiO_2 series of glasses were similarly prepared with the following quantities: 3.0 mL of methanol, 2.5 mL of TMOS, 0.5 mL of a 1% (by weight) methanolic solution of $E_T(30)$, 2.0 mL of a 8.2×10^{-2} M aqueous solution of CTAC + SDS (at various CTAC/SDS ratios, keeping (CTAC + SDS): Si $= 4.8 \times 10^{-3}$ constant), and 0.4 mL of water. Entrapment of the indicators without surfactant was performed as above, but with adding 1.0 mL of methanol instead of the 1.0 mL of the surfactant solution.

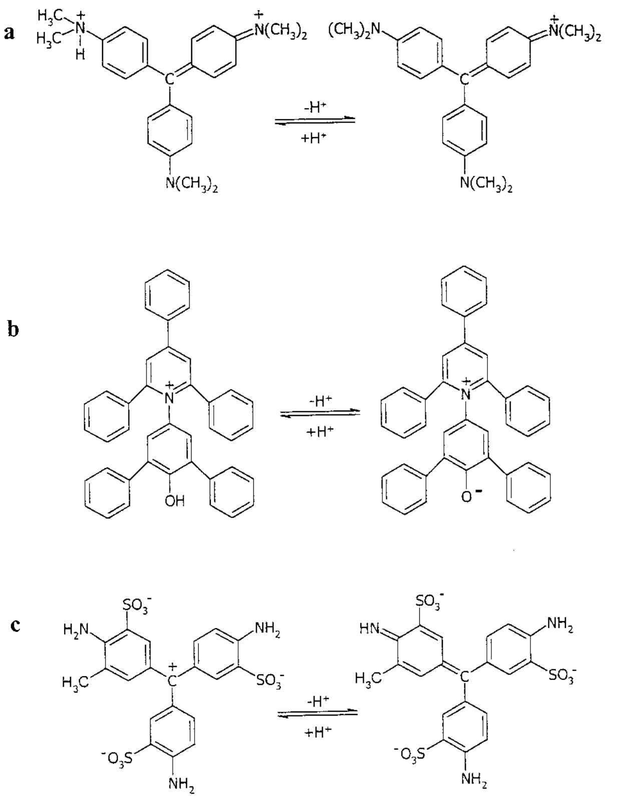

Figure 1. Protonated and de-protonated forms of the dyes used in this study. (a) crystal violet (CV); (b) 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)-phenolate ($E_T(30)$); (c) acid fuchsin (AF).

Isosbestic Points, Titration Curves and pK_i Values. The isosbestic points of CV were determined by taking full spectra each 15 s within the cell of an HP 8453 diode array UV/vis spectrometer. Full titration curves were obtained by taking solutions at various pH values, allowing the sol−gel glass to reach equilibrium (about 15 min), and by recording the relative absorptions of the basic/acidic forms.

Leaching tests for AF series were performed by placing the sol−gel glasses (with typical dimensions of about 8 mm × 10 mm × 1.5 mm, cut from the above-mentioned glasses) in 50 mL of an aqueous acidic solution at pH = 0.01, and taking the full spectrum every 24 h for 30 days.

Results

Preliminary Observations of the Effects of Various Surfactants on Crystal Violet. Our first dopant with which proved that, indeed, dopant properties can be differently affected by co-entrapment with surfactants of different nature, has been crystal violet (CV), which is a cationic dye (Figure 1a) with a pK_i value at the high acidity range of 1.0. Its co-entrapment with a series of surfactants—the cationic CTAB, the anionic sodium 1-dodecanesulfonate (SDS), the zwitterionic palmityl sulfobetaine (SB-16), and the nonionic Triton X-100 (TX-100), all within sol−gel silicas, produced the results shown in Figure 2a. Compared with the entrapment in pure silica or co-entrapment with TX-100 which shifted the pK_i to a slightly less acidic value, this shift was enhanced by co-entrapment with SB-16, and became as large as 3 orders of magnitude for the anionic SDS; more explicitly, the SiO_2/SDS system facilitates the protonation of CV-monocation (Figure 1a) at a hydronium concentration several hundred times smaller than needed in water. Figure 2a shows also that one surfactant, the cationic CTAB, is capable of shifting the pK_i to the other direction, namely to a higher acidity, actually to the edge of the logarithmic pH scale. As already noted in an earlier study,[4a] the breadth of

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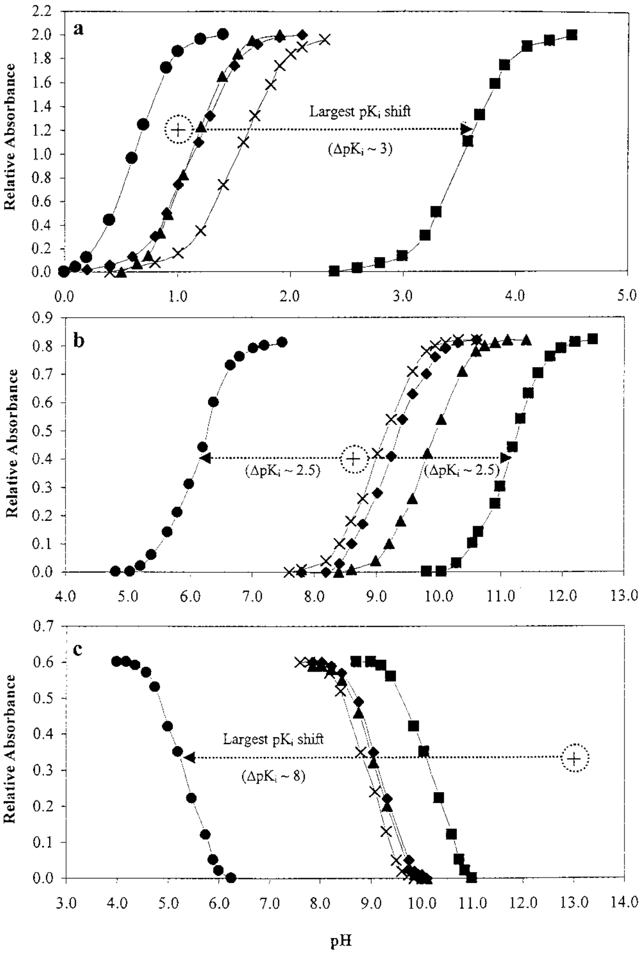

Figure 2. Titration curves of the dyes indicated in Figure 1, co-entrapped in silica sol−gel matrices with the surfactants TX-100 (▲), SB-16 (×), CTAB (●), SDS (■) and no-surfactant (◆). (a) CV; (b) E_T(30); c AF; value in solution (⊕)

the titration curves in these heterogeneous environments is wider than in solution.

Utilizing the CV Observations To Affect the Behavior of E_T(30). The facts that SDS and CTAB which are of opposite charges affect CV in opposite directions, that in terms of pK_i units, the anionic SDS has the largest effect on the cationic CV, and that the noncharged TX-100 does not alter the shift induced by pure silica suggested that of the possible interactions, the first-order effect is ionic, as proposed by Hartley for aqueous solutions.[7] We shall provide below a finer picture of these interactions; yet this first-order conclusion was sufficient to assume that if one wishes to attain for a specific compound the ability to cause *both* a large acidic pK_i shift and large basic one, then a zwitterionic indicator could be the answer. Its anionic portion would be affected by CTAB and its cationic moiety by SDS. This indeed proved to be the case with the zwitterionic E_T(30) (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)-phenolate[12] (Figures 1b and 2b). In solution, the pK_i is 8.6; with CTAB it becomes an indicator for the mild acidic range; and with SDS it becomes an indicator for the high basic range. *One molecule* is capable of detecting either acidity or basicity, separated by 5 orders of magnitude in hydronium concentrations as well as between values.

Utilizing the CV and E_T(30) Observations To Push the Effect to an Extreme. In an effort to push this pK_i shifting effect to an extreme, we turned next, using the same rational, to acid fuchsin (AF) because it carries three negative charges in both its protonated and deprotonated forms (Figure 1c). In solution, AF indicates very high pH values (~13), but co-entrapment with the counter positively charged CTAB shifted the K_i by 8 (!) orders of magnitude (Figure 2c), converting AF into an indicator for the *acidic* range. In other words, an increase in hydronium concentration of about 100,000,000-fold is now needed to cause this dye to change its color; the full power of this methodology in affecting molecular performance became thus evident. That the mechanism is more complex than provided by Hartley's rules which focus only on ionic interactions is clear from the pK_i shift affected by the anionic SDS, which in this case has the *same* direction as that of CTAB—we return to it below.[13]

Table 1. Properties of E_T(30) Co-entrapped with Several Surfactants and Surfactant Mixtures

surfactant entrapped	pK_i	color change[a]	λ_{max}[b] (nm)
CPB	6.0	Y-BR	540
CTAB	6.1	Y-BR	542
CTAC	6.2	Y-BR	539
CTApTS	6.5	Y-BR	550
SDS	11.1	Y-BR	512
CTAC:SDS (70:30)	10.3	Y-BR	521
CTAC:SDS (45:55)	11.9	Y-B	547
CTAC:SDS (30:70)	12.4	Y-BR	531

[a] Left color: acidic form, right color: basic form. B: blue, BR: brownish-red and Y: yellow. [b] The absorbance wavelength belongs to the basic deprotonated form. The acidic form absorbs in the UV range.

Fine-Tuning the pK_i through Small Variations in the Surfactant. Our next goal has been to add the feature of fine-tunability of the pK_i. This has been achieved in two ways. The first one was to utilize mild variations in a specific type of surfactant. This approach has been tested and demonstrated for E_T(30) using the four cetylammonium surfactants shown in Table 1. Indeed, as indicated in Table 1, fine-tuning in the 6.0−6.5 pK_i range was achieved.

Fine-Tuning the pK_i by Using Surfactant Mixtures. The results of the second approach for fine-tuning are, we believe, one of the main messages of this study: a mixture of two surfactants can be used for that purpose, as shown for E_T(30)/cetyltrimethylammoniumchloride (CTAC)/SDS in Table 1. Interestingly, the mixture shows synergism: SDS admixed with CTAC pushes the pK_i to values, which are higher than obtained for entrapped SDS alone (Table 1). Since the ratio of the surfactants can be varied at will, this is by far the easiest and most general way to extract a specific pK_i. Furthermore, calibration curves with surfactant mixtures will enable one to tailor and predict accurately a pK_i outcome. (Note, for instance, that CTAC/SDS compositions from 100 to 30% CTAC affect the pK_i from 6.2 to 12.4 almost linearly). Genuine, continuous variability in the pK_i, taking only one compound, has thus been achieved.

Discussion and Further Observations

The main purpose of this report has been the description of the methodology and the resulting phenomena. Yet their origin

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(13) The encapsulation within the sol−gel matrix provided also added stability for the dopant, as already observed in many doped sol−gel systems:[14] AF in CTAB and SDS solutions bleaches upon pH changes, and in fact, none of the three dyes used in this study serve routinely as a pH indicator for aqueous solutions.

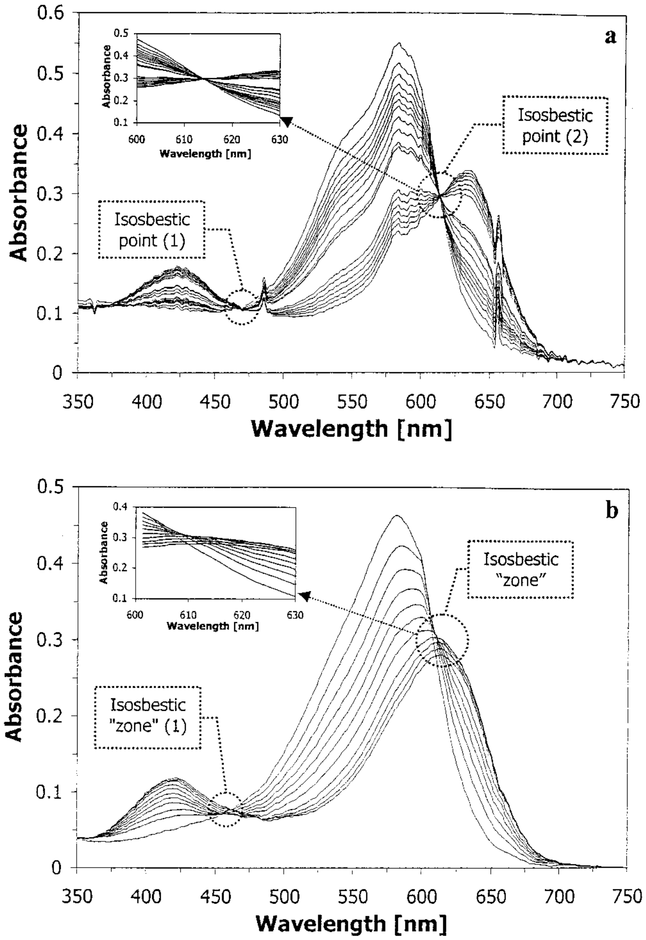

Figure 3. Entrapped surfactant effects on the isosbestic points of CV: For SDS (a) this point is very sharp while for CTAB (b) it drifts with the pH, indicating migration of CV within the microheterogeneous cage.

is so intriguing that we offer now some interpretations and the results of additional measurements. For brevity reasons we shall focus here on CTAB and SDS, and these will show the direction toward similar arguments regarding the other surfactants. Let us begin then with our first example, CV. Why do these surfactants shift the pK_i; and why in opposite directions? One of two first-order causes was mentioned above: the specific nature of the ionic interactions between surfactants and indicator. To this we add now the second major cause, namely the location of the molecule in the microheterogeneous environment and its pH-induced migration into and out of the hydrophobic or polar zones of the caged pseudomicellar domains, the existence of which was proved in great detail in ref 1 (see also ref 10). Since protonation/deprotonation of the molecule causes changes in its polarity and hydrophobicity, this change is a driving force for the molecule to reorient its location to compatible domains within the heterogeneous environment. The effect of the ionic interactions and how they differ between SDS and CTAB, are nicely seen in the 612 nm isosbestic points of CV (Figure 3): For SDS this point is very sharp, while for CTAB it drifts with the pH. SDS, being in its anionic form even at low pH values (Figure 2a), complexes strongly[8,15] with the two cationic forms of CV (Figure 1a), and this strong association maintains CV in the same immediate environment throughout pH changes. On the other hand, since both CV and CTAB are cationic, strong ionic surfactant/indicator interactions are not operative here, and CTAB becomes prone to the gradual changes in the environment which are affected by the pH changes (ionic strength, protonation of silanols, the structure of the confined water, the charge density of the Stern layer, to mention a few). Thus, each point along the whole titration curve is affected by the environment, to a different extent. Reorientation of CV as it changes its charge is evident from the acidic shift caused by CTAB. The mono and dication of CV (Figure 1a) differ in their affinity to the cage domains. While the polar dication must reside in the most polar regions of the cage, exposed to the aqueous layers at the silica cage interface, the more hydrophobic monocation is partially buried within the more hydrophobic micellar domains. Consequently, CV^+ is less accessible to hydronium ions, and protonation to CV^{2+} to reach pK_i conditions in the immediate environment of the molecule requires higher external H_3O^+ concentration. The interpretation that the observed pK_i shifts do not reflect inherent changes in the equilibrium constant but external conditions which are needed to compensate for local effects within the cage is general and applicable to many of the other observed shifts. In fact, not only burial within hydrophobic regions is responsible for the needed changes in the external pH, but also local (high or low) concentrations of H_3O^+ induced by the charged layer of the pseudomicelle. For CTAB, the cationic interface make it more difficult for H_3O^+ to penetrate, adding to the need of higher external acidity.

The opposite is true for SDS, which holds both CV^+ and CV^{2+} tightly at the micellar SO_3^- interface, which also acts as a proton sponge.[16] This action increases significantly the local concentration of H_3O^+, in synergism with the silanol groups through associations such as $SiOH\cdots H_3O^+\cdots SO_3^-$ and even $SO_3^-\cdots H_3O^+\cdots SO_3^-$ (because the pK_i of silica is around 2^{17}). The exposure of CV to this local higher concentration of H_3O^+ (in fact, by a factor of about 1000), causes the pK_i to appear at much weaker external acidities. Thus, again, the fact that in the presence of SDS entrapped CV appears to be a weaker acid is not because the acidity constant of CV changes by 3 orders of magnitude but because the entrapped indicator reports on the modified *external* pH needed to achieve the $pH = pK_i$ value in the immediate CV environment.

Similar arguments are applicable for other entrapped indicator/surfactants pairs. For instance, the particularly large effect of CTAB on AF is understood in terms of its strong association with the three sulfonate groups of the AF molecule. Thus, Bunton et al. showed[18] that the aryl-sulfonic moieties penetrate the Stern layer of cationic micelles in a sandwich-like arrangement. It follows that high proton concentrations are needed both to compete with the surfactant/indicator interaction and to overcome the repulsion from the positive ammonium layer. The effect of SDS on AF, which is contrary to Hartley's rules,[8,9] shows that these rules may be too simple to account for the behavior at the materials' cages interface. It seems plausible that the shift to higher acidity for SDS is again a reflection of its ability to act as a proton sponge.

The solvatochromic nature of $E_T(30)$ [12] can signal its specific location in a micellar environment.[19] Likewise, the λ_{max} values of the sol−gel entrapped $E_T(30)$ can be used for deduction of its location within the cage. With CTAB the value is 542 nm,

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while with SDS it drops to 512 nm. Using the $E_T(30)$ scale, this indicates an increase in the local polarity probed by the dopant, by changing from CTAB to SDS (polarity depends inversely on λ_{max} for this probe[12]). These values, which resemble those of the lower alcohols (from 564 nm for 1-propanol to 515 nm for methanol) provide a further hint as to the apparent relative locations of $E_T(30)$. While the negatively charged layer of SDS is capable of attracting and pulling out the hydrophobic triphenyl cation nearer to the polar silica−water interface, the positively charged layer of the cationic CTAB repulses it partially back into the hydrophobic core. NMR measurements[20] indeed indicated that $E_T(30)$ arranges itself spatially inside the micelle but near its interface so that the main interaction is between one of its zwitterionic charges and the opposite charges on the outer micellar layer. Interestingly, these two entrapped surfactant systems also corroborate our earlier observation,[1] that the amphiphilic nature is enhanced by the sol−gel entrapment: The pK_i's in CTAB and in SDS solutions[19] are pushed to more acidic or basic values, respectively, by about one pK_i unit upon entrapment. Finally, we are not ready yet to provide an explanation of why admixing SDS with CTAC enhances the effect of the former on $E_T(30)$ (Table 1).

Further Consequences and Conclusions

The ability to control the acid/base properties of the dopants with heterogenized solid-state micelles points the way for affecting other molecular and material properties. An example for a useful application is the control of the release rate of entrapped molecules.[21] The specific hypothesis, tested for AF, was that co-entrapment with a surfactant with a similar charge will help to expel the dopant out, while encasement with a surfactant with opposite charge will prevent leaching and effectively anchor the molecule inside the matrix. Figure 4 indeed shows that the leaching rate from the pure sol−gel matrix (half-life of 7 months, based on first-order analysis) is accelerated to 3 months with SDS, slowed to 2.5 years with the zwitterionic SB-16, and is practically stopped with CTAB (17 years). Although not carried here, one can envisage again the possibility of fine-tuning of the release rate with surfactants mixtures, as demonstrated for the pK_i's. We note that controlling and fine-tuning of release by standard methods requires usually elaborated tempering with the matrix itself. We believe that the convenient "off-the-shelf solid micelles" will find more applications.

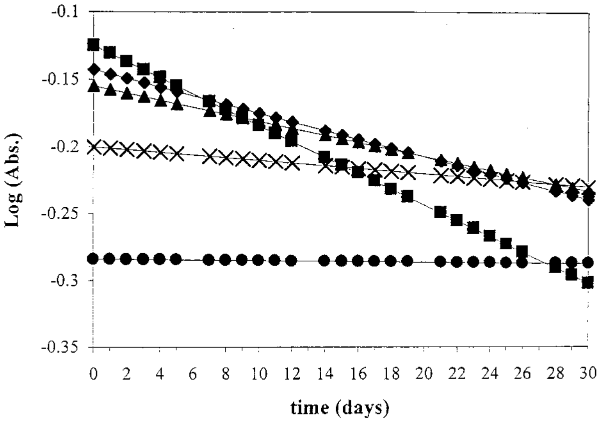

Figure 4. Control of the release rate of AF from a solid matrix by encasing it with various surfactants: TX-100 (▲), SB-16 (×), CTAB (●), SDS (■) and no-surfactant (◆).

Finally, a more general outlook is offered here:. We are used to viewing a given compound as providing a typical, narrowly defined performance (such as indicating a specific pH value). However, we show here that a single compound can be viewed in broader terms as carrying a potential library of reactivities which can be realized by properly tailoring a heterogeneous microenvironment. Thus, a consequence of this broadening of view is the ability to tailor "dream" molecules from ordinary ones.

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