

Photoinduced electron transfer between molecules in silica matrices

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Abstract. The reactions of electron transfer between anthracene (An), pyrene (Py) and fluorescence quenchers N,N-dimethylaniline (DMA), N,N-diethylaniline (DEA) and Cu^{2+} ions in heterogeneous systems on the basis of silica under the conditions of differing mobilities of molecules and changes of carrier structure have been studied. Quenching of An^* and Py^* by DEA and DMA on adsorption from hexane on the surface of pyrogenic nonporous silica-aerosil is accompanied by exciplex formation and concentrational dependence of the rate constant of quenching. Fluorescence of solubilized Py is quenched very strongly by adding DMA in adsorbed TX-100 micelles. Removal of water sharply changes the photonics of the system. Intensity of Py fluorescence remains high and no quenching occurs. Py molecules are encapsulated in the SiO_2 between layers of hydrophobic parts of TX-100. Photoinduced electron transfer between Py^* and Cu^{2+} is effective at the stage of sol-gel transition in tetraethoxysilane (TEOS) hydrolysis reaction. Py molecules trapped in porous sol-gel phases are shown to undergo photoinduced electron transfer with Cu^{2+} when the liquid phase is present inside the pores.

Keywords. Exciplex; adsorption; electron transfer; silica.

1. Introduction

The introduction of photoreactive molecules into a dispersed oxide composition is an attractive way to create light-transforming photosensitive systems with a wide set of unique spectral properties. Various promising applications of these novel materials include photochromic systems, lasers, light guides etc. Photoinduced electron transfer and charge separation in heterogeneous media can be enhanced by the process of adsorption and incorporation of the guest molecules (de Mayo *et al* 1985; Kalyanasundaram 1987; Thomas 1987, 1993; Anpo and Matsuura 1989; Birenbaum *et al* 1989; Eremenko 1989; Yakimova *et al* 1989; Eremenko *et al* 1990; Gafney 1990; Krasnansky *et al* 1990; Ramamurthy 1991; Samuel *et al* 1991; Kamat 1993). Of particular interest are the photochemical bimolecular charge transfer processes on inorganic oxide surfaces. Studies on the formation of excited molecular complexes (exciplexes) are extremely important from the point of view of elucidating the mechanism of not only photochemical but also chemical reactions based on electron transfer. Difficulties in investigating intermolecular processes activated under UV-irradiation in solid state heterogeneous matrices (e.g. SiO_2) are due to limitations of molecular mobility, coexistence of different kinds of adsorbate interaction with the surrounding medium, the change of photoprocess direction etc. Self-organized systems such as micelles have a similarly charged or

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neutral interface. This work deals with investigation of bimolecular reaction of electron phototransfer in heterogeneous media on the basis of silica under conditions of differing mobilities of molecules and changes in the aggregate state of the carrier. Reactions of electron phototransfer are considered: (1) in exciplexes of anthracene – N,N-diethylaniline (DEA) (An-DEA) and pyrene – N,N-dimethylaniline (DMA) (Py-DMA) – under adsorption conditions on the surface of non-porous silica-aerosil (AS); (2) by solubilization of a Py-DMA pair in micelles of a nonionic surfactant TX-100 under adsorption condition on AS; (3) quenching of an excited Py with Cu^{2+} ions in a stage of sol–gel–xerogel transition in the reaction of TEOS hydrolysis and formation of glasslike silica. The first case offers the possibility of a free diffusion of molecules along the surface, and the remaining ones permit limited movement in organized media. In the latter case, the use of a tertiary amine as a quencher was excluded due to the possibility of full protonation of DMA in the reaction of TEOS hydrolysis by molecules of a polysilicic acid.

2. Experimental

Materials: The pyrogenic nonporous high disperse silica, A-300 trade mark, $S_{sp} \cong 260 \text{ m}^2/\text{g}$, was annealed prior to adsorption for 5 h at 773 K. The amount of impurity did not exceed 0.01 wt.% (by emission analysis). Spectrally pure Py was recrystallized additionally from ethanol and purified by zone melting. Spectrally pure DEA and DMA were exposed to vacuum distillation and kept in sealed ampoules. Solvents were purified by distillation over molecular sieves by known procedures. Triton X-100 (Lachema, Czechia) was used without additional purification. Adsorption of Py and DMA was done from solutions in hexane and TX-100 in water followed by spectrophotometric control with Specord M-40.

Solubilization of Py and DMA in micelles: Respective solutions of Py and DMA in hexane or in a molecular form (weighted amounts of Py crystals and liquid DMA) were added to an aqueous micellar solution of TX-100 at a concentration of $3.2 \times 10^{-2} \text{ M}$ and mixed by a magnetic stirrer for 8 h.

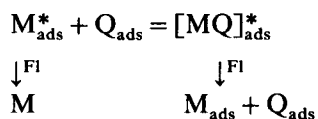
Sol-gel systems: For preparation of sol–gel systems the hydrolysis of the alcohol solutions of TEOS (Aldrich) was effected by the presence of HCl as a catalyst (Iler 1982; Avnir et al 1985; Kaufman et al 1986).

Luminescence: Stationary fluorescence spectra were recorded using an SDL-2 spectrofluorometer with excitation from a xenon lamp. The kinetics of fluorescence quenching was measured with a laser fluorometer with pulse nitrogen laser excitation at $\tau_{im} = 10 \text{ ns}$.

3. Results and discussion

3.1 Interaction fluorophor-quencher on AS surface while sorbing from hexane

The formation reaction of An-DEA and Py-DMA exciplexes on the surface of a nonporous support,



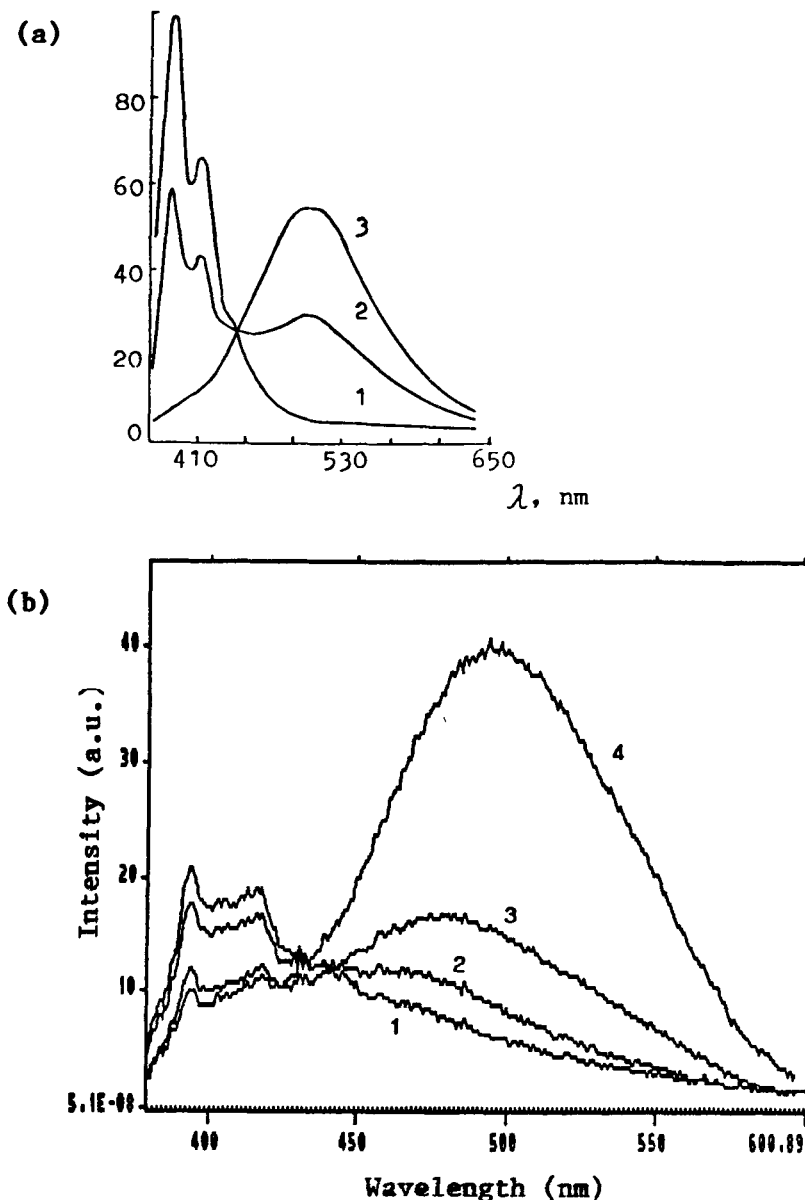


Figure 1. Luminescence spectra of An/DEA (a), and Py/DMA (b) on SiO₂, on adsorption from hexane, σ % from monolayer. (a) An 0.06 (1–3); DEA 0(1); 10 (2); 100 (3). (b) Py 0.5 (1–4); DMA 0 (1); 0.4 (2); 4 (3); 40 (4).

is subject to the influence of the aerosil due to bonding of the first portion of the amine, and the formation of a “quenching sphere”. The excitation spectrum of An-DEA coincides with the absorption spectrum of An with an accuracy of $\pm 1 \text{ cm}^{-1}$ (Yakimova *et al* 1989). In the coverage range of $< 0.1\%$ of monolayer, τ is not affected by addition of quencher, which is due to its chemisorption on acid OH groups and non-participation in the excimer formation process. Figure 1 gives the emission spectra

Table 1. τ and Kq An and Py on the aerosil surface in presence of quencher (DEA and DMA respectively),

An (%)	DEA (%)	τ (ns)	$K_q (\times 10^{10})$ (L/M s)	Py (%)	DMA (%)	τ (ns)	$K_q (\times 10^8)$ (L/M s)
0.06	—	8.22		0.5	0.4	260	4.6
0.06	10	3.62	5.7	0.5	4	145	1.5
0.06	100	3.32	3.7	0.5	40	135	18

of An/DEA/AS and Py/DMA/AS. Luminescence of the Py/DMA exciplex on aerosil with increased concentration of the quencher is shifted by 20–25 nm into a long-wavelength range (emission maxima are stable for An/DEA). This is evidence of localization of Py/DMA exciplex in an area of relatively high polarity on the aerosil surface and of higher sensitivity of this pair to the polarity of surroundings as compared to An/DEA.

The difference may be explained by the large lifetime of Py during which the position of the Py/DMA exciplex on the surface is changed. Rate constants of quenching depend on quencher concentrations on the surface (table 1). In the Py/DMA adsorption system Kq is markedly lower than diffusional; for the An/DEA pair the constants are close to observed ones in a hexane solution. A process of exciplex formation on the surface includes diffusion collision of components, followed by a charge transfer, and their mutual orientation. While analyzing variations of Kq with the adsorption value of a quencher, one should take into account the inhomogeneity of its distribution over an energetically nonuniform aerosil surface. For both EDA pairs, Kq decreases with increase in σ of a quencher; for Py/DMA this value approaches values typical of kinetically controlled reactions. For large adsorptions the possibility of forming "aggregate pairs" of the Van-der-Waals complex type is not excluded, having a favourable geometry for formation of the exciplex. Lowering the temperature of recording to 77 K and 4.2 K (An/DEA/AS) results in disappearance of the exciplex luminescence (which confirms the diffusional mechanism of its formation). The structural spectrum of An changes (Yakimova *et al* 1992), its broadening and long-wave shift correspond to the behaviour of anthracene in the polar solvent. The lifetime of An at 77 K is decreased two-fold. Moreover time-resolved spectra provide evidence for An aggregate formation with decreasing temperature. These facts seem to be connected to peculiarities of the An distribution on the surface modified by amine aerosol whose polarity is changed with temperature. Spectra of Py/DMA/AS fluorescence are broadened as temperature decreases and are, probably, a superposition of the fluorescences of Py monomer and exciplex. It is noted in Mataga (1981) that Py in a DMA medium forms weak heteroexciplex even in a solid glass-like matrix, with a fluorescent band shifted strongly into a short wavenumber region. That is to say, the orientation necessary for exciplex formation is carried out in a ground state. This is evident from low Kq values (table 1). Differences in kinetic parameters of a photoinduced electron transfer in bimolecular reactions of An and Py on the AS surface also seem to be due to differences in adsorption values of fluorophores and their lifetimes.

3.2 Interaction of Py/DMA in micellar solutions and in micelles of TX-100 on the SiO₂ surface

There are very few studies on the formation of exciplexes in micellar solutions (Kalyanasundaram and Thomas 1977; Almgren and Lofroth 1981; Kikushi and Thomas 1988; Borsarelli *et al* 1993). Quenching of pyrene derivatives in ionic micelles by molecules of N,N-dimethylaminosulfonate does not obey the Stern–Volmer equation but runs much more strongly, and excimer luminescence is not observed. Kinetics of the quenching process is determined by the rate of quencher entering the micelles and the diffusion of the fluorophor in a micelle core. When solubilized in a solution of 2% TX-100, exciplex Py/DMA is formed for a higher DMA concentration than in hexane (the ratios of DMA/Py are 80:1 and 4:1 respectively). The position of the maximum of exciplex fluorescence in TX-100 (510 nm) is close to that obtained on SiO₂ and evidence is in favor of a sufficiently high polarity of surrounding in the micelle. The polarity of an intermicellar surrounding of Py/DMA estimated by extrapolation of the dependence relation between the maximum energy of dansyl dodecylamine (DDA) fluorescence and the parameters of solvent polarity in various surfactants (Gafney 1990), gives the value of dielectric constant inside TX-100, $\epsilon = 30\text{--}32$. The average number of DMA molecules in the micelle was estimated by kinetics of fluorescence decay as

$$F(t) = F_0 \exp[-t/\tau_0 + n(e^{-kt} - 1)],$$

where $F(t)$ is intensity of luminescence at time $t = 0$, τ_0 is lifetime of Py in micelle without quencher, n is average number of quencher molecules in the micelle. At $t \rightarrow \infty$ one obtains $F(t) = F_0 e^{-n} e^{-t/\tau_0}$. At concentrations of Py, DMA and TX-100 equal to 2.5×10^{-4} M, 10^{-2} M, and 3.2×10^{-2} M respectively, $n = 2.69$ per micelle. Calculation of the actual amount of DMA present gives a value of 30 molecules per micelle. Thus, < 10% DMA takes active part in the process of quenching, the remaining mass seems to be adsorbed on the micelle–water boundary and bonded to the ester groups by an oxyethylene linkage. The number N of TX-100 aggregates in the solution is estimated from n and the real DMA concentration $[Q]$,

$$N = n[\text{TX-100}]/[Q],$$

and is about 100, which is close to values reported in Mataga (1981).

3.3 Luminescence of Py-DMA exciplexes in TX 100 micelles under adsorption conditions. Reconstruction of aerosol structure

Using microcalorimetry and decay of Py fluorescence Borsarelli *et al* (1993), Kalyanasundaram and Thomas (1977), Denoyel and Rouquerol (1991), and Levitz and Van Damme (1984, 1986) have shown a cooperative mechanism of TX-100 adsorption on three silica types including aerosil. At low concentrations, TX-100 is sorbed by oxyethylene linkages interacting with the OH-groups of the aerosil simultaneously, and at high concentrations, aggregation of surfactant molecules on the surface occurs. Connections of initial solutions of TX-100 ensure, according to Borsarelli *et al* (1993), and Kalyanasundaram and Thomas (1977), a complete coating of the aerosil surface by coalescing TX-100 micelles containing solubilised molecules of reagents. If water is not removed from the Py/DMA/TX-100/SiO₂/H₂O system, photochemical behaviour of Py and exciplex in such gel-like compositions (semitransparent gel) is similar to their behaviour in micellar solution (figure 2). Luminescence intensity of the exciplex lowers

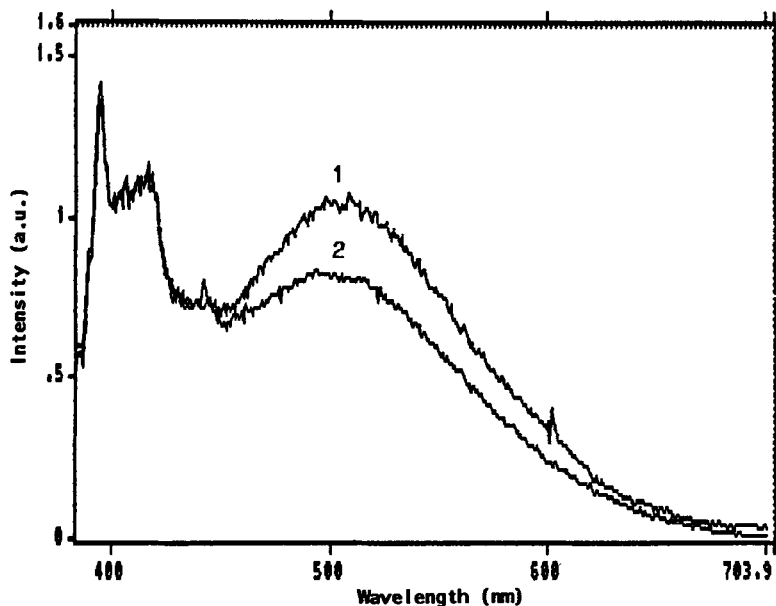


Figure 2. Luminescence spectra of water suspended system Py/DMA/TX-100/SiO₂. Concentrations M: Py – 2.5×10^{-4} ; DMA – 2×10^{-2} ; TX-100 – 3×10^{-2} , freshly prepared (1), 48 hours later (2)

somewhat two days after preparing the suspension; after this the spectrum remains unchanged. Kinetic characteristics of pyrene fluorescence decay are also close to these for an aqueous-micellar solution of Py/DMA/TX-100/H₂O (figure 3). When irradiated, the exciplex forms inside a micelle held with adsorption forces on the surface. Mechanisms of exciplex formation when micelles are present or absent are undoubtedly different. The limited space in a micelle core gives rise to conditions for more intimate contact of interacting molecules than in free diffusion of the molecules along the surface where there is no surfactant. Increased viscosity inside a micelle can influence the mechanism of exciplex formation. Usually, micelles of nonionic surfactants induce some retardation of quencher movement to a probe (Kalyanasundaram and Thomas 1977). A portion of DMA is held with OH groups of an oxyethylene linkage on the outer surface of the micelles. It is possible that some of the molecules form the exciplexes under conditions similar to static ones, their localizations being favorable in the ground state. Similar interaction is discussed for a pyrene-DMA pair in liquid-crystalline solvents (Kapinus and Malkin 1994). Piuze *et al* (1994) explain the different rates of photoinduced charge transfer as due to the existence of isomeric forms of the exciplex. These calculations lead to the consideration that exciplexes are formed with configuration differing from a sandwich-like one in a limited inner micellar space. Direct influence of the aerosil surface in the aqueous gel-like suspension of Py/DMA/TX-100/SiO₂/H₂O on photoprocesses in the micelle is absent (table 2). Under conditions of vacuum drying of Py/DMA/TX-100/SiO₂ samples at room temperature, removal of the intermicellar water abruptly changes the photonics of the system. The luminescence of exciplexes disappears in the spectra and Py quenching by DMA molecules does not take place at all (table 2). The emission spectrum consists of fluorescence of pyrene monomers for all concentrations of DMA. Addition of water or

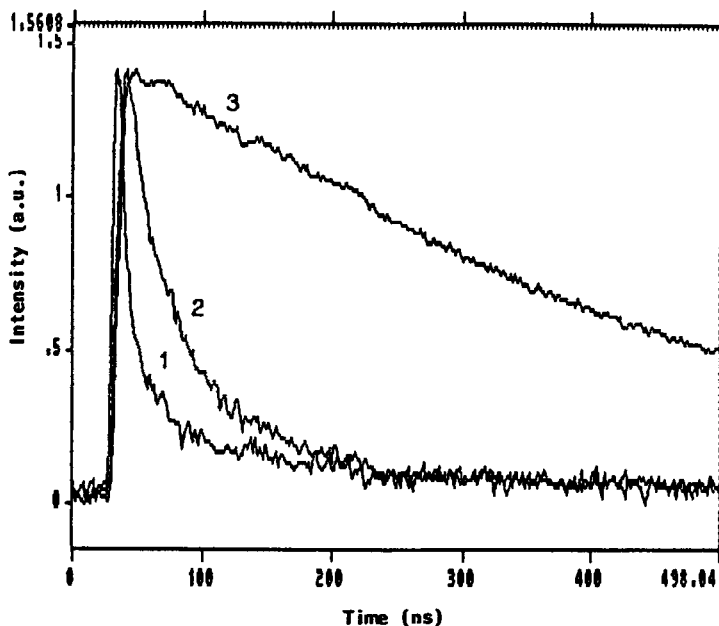


Figure 3. Decay of Py* fluorescence monitored at 395 nm in the systems: (1) Py/DMA on SiO₂ (adsorption from hexane) $\sigma\%$ Py-0.5/DMA-40; (2) Py/DMA/TX-100 at M $2.5 \times 10^{-4}/10^{-2}/3.2 \times 10^{-2}$ respectively; the same for Py/DMA/TX-100/SiO₂/H₂O (3) Py/DMA/TX-100/SiO₂ after drying $\sigma\%$ 0.5/40/100.

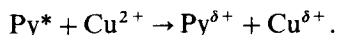
Table 2. Lifetimes for the decay of Py* luminescence by DMA in solution of TX-100 and in micelles of TX-1900 on silica and quenching rate constants K_q .

Py in TX-100 water solution, $c = 2.5 \times 10^{-4}$ M			Py in TX-100 on SiO ₂ after water removal, $c = 5 \times 10^{-6}$ mol/g	
DMA (M)	τ_{Py} (ns)	$K_q (\times 10^8)$ (M ⁻¹ S ⁻¹)	DMA (mol/g)	τ_{Py} (ns)
0	310		0	490
10^{-4}	205	5.16	2×10^{-6}	490
10^{-3}	266	5.32	2×10^{-5}	461
10^{-2}	65	0.122	2×10^{-4}	435

excessive DMA to the system after vacuum drying does not alter the spectral shape. Irreversible structural and chemical changes thus appear in the system. When pyrogenic silica is present in the aqueous TX-100 solution, a colloidal sol forms, and on drying, a process of sol-gel-xerogel transformation occurs which is accompanied by change in the structure and dispersion of the aerosol. When there is no water, micelles become disrupted and form aggregates of surfactant molecules on the surface. Hydrophobic Py molecules entrapped between layers of the hydrophobic portion of TX-100 are encapsulated in a SiO₂ gel after drying and become inaccessible to molecules of the quencher.

4. Quenching of Py luminescence by Cu^{2+} ions in the sol-gel-xerogel transition of silica

Information on an interaction between a molecule of Py and a copper ion is scarce in literature. Excited molecular compounds between Py and Cu^{2+} are interesting since between their components act forces of an electrostatic repulsion rather than attraction. Both components bear a positive charge,



Yield of cation-radical of pyrene in its reaction is 0.68 (Nosaka *et al* 1981). Stability of such formations is possibly due to an entropy factor (Loufer *et al* 1985). When Py and Cu^{2+} ions are incorporated into initial solutions of TEOS, absorption spectra register redistribution of intensity in the vibrational pyrene structure (figure 4), without appearance of new bands. Variations of τ with time of maturation (table 3) indicate that the sol-gel transition is completed in 10 minutes under given conditions. Low values of Kq seem to be due to relatively high concentration of the quencher in the sol and the possibility of formation of closely spaced Py/ Cu^{2+} pairs in the gel. In fact, after drying of this hydrogel, Py fluorescence in the xerogel has been quenched completely. Decrease in the Cu^{2+} concentration up to $C = 10^{-3} \text{ M/L}$ in the initial solution leads to Kq values that are more typical of diffusion-controlled reaction ($2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$); in so doing, a jump of variation occurs at the 10th minute of the hydrolysis reaction – namely, at a moment of the sol-gel transition. At the functional group level, three reactions are generally used to describe the sol-gel process: etherification, alcoholysis, and hydrolysis. A polymerization process then begins with formation of cyclic, three-dimensional and other polymer varieties – immediate precursors of colloid particles (Iler 1982). This transition appears to fix Py quenching by Cu^{2+} ions in the system at their diffusional approach. The viscosity of such colloid particles increases sharply compared to the solution, and diffusion of Cu^{2+} occurs not in the solution of polysilicic acid but in the intermicellar liquid in a hydrosol medium. Similar processes of quencher movement in an intrapore

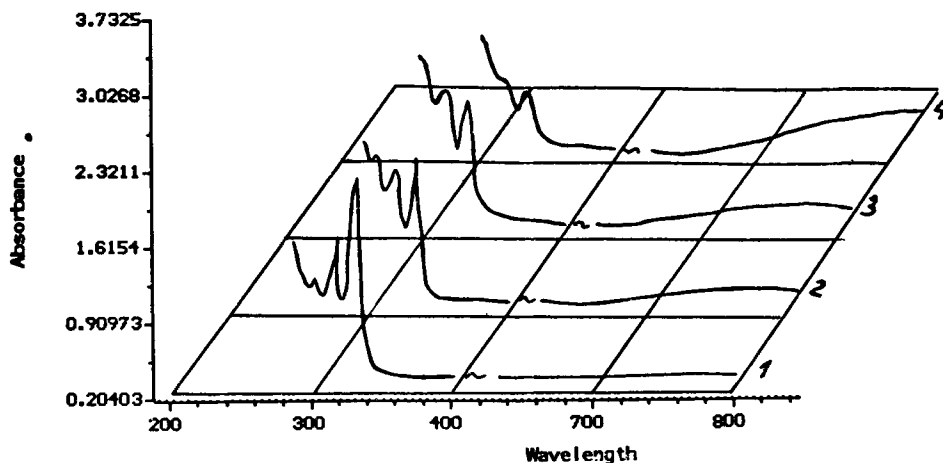


Figure 4. Absorptional spectra of Py $5 \times 10^{-5} \text{ M}$ in water-ethanol solution of TEOS containing Cu^{2+} ions, M (1) 5×10^{-2} ; (2) 10^{-1} ; (3) 1.5×10^{-1} ; (4) 2×10^{-1} .

Table 3. Dependence of τ_{py} and K_q on time maturation of Py/Cu/TEOS sol by content M:Py = 1.4×10^{-5} and Cu = 6×10^{-2} ; pH = 6.

Time of maturation	τ_{av} (ns)	$K_q (\times 10^8)$ ($M^{-1} s^{-1}$)
30 s	7.7	
2 min 30 s	11.2	2
6 min 11 s	10	0.93
10 min 45 s	49	0.20
33 min 15 s	51	0.19
60 min	50	0.20
150 min	50	0.20

liquid phase are discussed for glasses formed (Slama-Schwok *et al* 1991). No change in τ takes place during the next two weeks that seems to be indicative of invariability of hydrogel structure. Removal of the intermicellar liquid while drying the hydrogel at 90° for 5 h is accompanied by a sharp increase in the time of Py decay (for the system with a lower content of Cu^{2+} ions $\tau_{py} = 327$ ns). When the dried xerogel is soaked in the alcohol, a diffusion of Cu^{2+} in pores is restored, a quenching of Py occurs, and τ falls to 63 ns. When concentration of Cu^{2+} increases after drying of the sample and formation of the xerogel, luminescence of Py is completely quenched, seemingly because of the formation of a "quenching sphere" at an intimate contact Py with Cu^{2+} ions (Nosaka *et al* 1981; Liu *et al* 1989). Thus, the mechanism of quenching allows long-range electron transfer. Analysis of our results leads to the suggestion of Py quenching in contact with Cu^{2+} ions by diffusion. Dependence of the vibrational Py structure on concentration of Cu^{2+} is noticed in the absorption spectra of initial solutions of Py and Cu^{2+} in TEOS (figure 4) which is evidence of the influence of hydrated copper ions on the electronic shell of pyrene molecules.

5. Conclusion

All the presently investigated redox pairs show photoinduced electron transfer between the molecules as well as those adsorbed on the silica surface, on the surface of solubilized micelles or trapped in sol-gel glass. The quenching proceeds mainly by the diffusion mechanism in the surface layer of the aerosil; when Py content of a monolayer increases from 0.06 to 0.5%, some contribution from statical quenching to a "sphere" is possible. Chemisorption of some of the quencher molecules on the aerosil surface is noted. On solubilization of Py/DMA in micelles adsorbed on the SiO_2 surface, the quenching takes place within the limited space of the micelle and is not influenced by the surface. Exciplex Py/DMA in the micelle is formed for a higher DMA concentration than in hexane. Removal of the intermicellar liquid sharply changes the photonics of the system because irreversible structural and chemical transformations take place in the aerosil.

Changes in the process of sol-gel transition in the hydrolysis of TEOS are followed by quenching of Py^* by Cu^{2+} ions, and a step in the sol-gel transition has been established. Molecules incorporated in the xerogel of a silicate glass take part in the photoreaction only in the presence of the intermicellar liquid, ensuring diffusion in the pores.

Research along these lines is in progress in our laboratory.

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