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Energy Transfer Between Aromatic Hydrocarbons Dissolved in a C18-Surfactant Layer Adsorbed on Laponite

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Abstract. The energy transfer between pyrene and perylene was studied in a system in which the hydrocarbons were dissolved in the surfactant layer adsorbed on the surface of an organoclay prepared by rapid mixing of Laponite clay and a C18 surfactant. The experimental quenching data gave critical energy transfer radii of 53.3 Å. A theoretical calculation of this radius using the Förster approximation indicated a value of 53 ± 7 Å for this interaction. All these values were in good agreement with similar experiments for the energy transfer between the hydrocarbons in organic solvents. Furthermore, the ratio I_1/I_3 of the intensities of the vibronic fine structure of the emission spectrum of pyrene in this system was found to be 1.25, similar to the value found for the same probe in several surfactants, indicating that pyrene is localized in the organic layer.

Keywords: clay-surfactant interactions, energy transfer, hydrocarbon adsorption

Introduction

The understanding of the function that clay surfaces play in many processes justifies the great number of studies concerning the properties of these materials. Its use as an active agent on catalysis processes, as adsorbents, support agents, fillers, paper coating and foundry moulds, demonstrates the versatility of this material (Grim, 1968; Thomas, 1982). The properties that make clays interesting materials for all these different purposes are their very high specific surface area (~750 m^2/g) and surface polarity (van Olphen, 1977). The surfaces can be easily modified by the exchange of the cations originally present on their structure (usually Na^+) by other inorganic cations like polioxications to form pillared clays (Petridis et al., 1996; Fetter et al., 1997), as well as by organic cations, like alkylammonium quaternary salts, leading to organoclays (Sheng et al., 1997; Boyd et al., 1988; Favre and Lagaly, 1991; Lagaly, 1981; Ogawa et al., 1993; Sheng et al., 1996; Tahani et al., 1999; Breen and Watson, 1998; Ferreira et al., to be published; Della Guardia and Thomas, 1983; Liu et al., 1989).

The investigation of factors like the mobility of probes in the clay environment and their accessibility to the internal surfaces of the particles gives important information about the role that the organized media play in chemical reactions. Additionally, the study of specific interaction between probes and active sites present on the surfaces may give a better insight into these processes.

In previous studies with organoclays carried out in our laboratory (Ferreira et al., to be published) it was found that relative simple experimental controls allow the preparation of organoclays with specific properties. It was proved that the characteristics of the organoclays depend mainly of three factors: type of clay used, length of the alkyl chain of the surfactant and experimental method used to prepare the organoclay.

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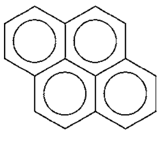
The aim of this paper is to investigate how the surface of a specific type of organoclay (C18-Laponite) influences the energy-transfer process between aromatic hydrocarbons and, thus, indirectly give information about the media created by the organic phase on the surface of the organoclay. Pyrene and perylene were used to study the singlet-singlet energy transfer processes in these systems. The same pair of hydrocarbons has been largely used in the study of energy-transfer in solution as well adsorbed on other surfaces like zeolites (Iu and Thomas, 1990; Liu et al., 1989) and silica (Marro and Thomas, 1993).

Materials and Methods

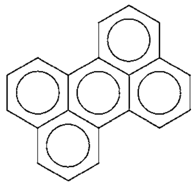
Chemicals

The clay used in the experiments was Laponite B, a synthetic Hectorite (Laporte Ind., UK; see properties in Table 1, van Olphen and Fripiat, 1979). This clay was purified as described in an earlier work and left in the Na^+ homo-ionic form. (Gessner et al., 1994).

The aromatic hydrocarbons used were pyrene (Aldrich, recrystallized twice from methanol) and perylene (Aldrich, used as received). The surfactant octadecyltrimethylammonium bromide (C18, Fluka) was used as received. Benzene (Merck, p.a. grade) and Milli-Q deionized water were used as solvents.



pyrene (Py)



perylene (Pery)

Instruments

Fluorescence emission spectra were recorded on a Hitachi F-4500 Spectrofluorimeter, using a front-face sample set-up. The fluorescence quantum yields of the probes adsorbed on the solid samples were determined on a Cary 5G UV-vis-NIR spectrophotometer using an integrating sphere. Fluorescence lifetimes were measured at room temperature by time-correlated single-photon counting using an Edinburgh CD-900 instrument. The fluorescence decay profiles were analyzed with a non-linear least-squares iterative re-convolution method. Excitation of the probe was always performed at 340 nm and the detection wavelength was 390 nm.

Preparation of the Organoclay (C18-Laponite)

An experimental procedure to prepare organoclays with specific characteristics has been developed in our laboratory (Ferreira et al., to be published). To prepare samples in which the surfactant molecules are preferentially adsorbed on the external clay surfaces, 200 mL of a saturated solution (2.6 g/L) of octadecyltrimethylammonium bromide (C18) were added to 2000 mL of a 2 g/L aqueous suspension of Laponite. The addition of the surfactant solution to the clay suspension was done at once, under vigorous stirring. After some minutes, this clay-surfactant suspension flocculated and was filtered under vacuum and washed with approximately 500 mL of deionized water. This procedure renders an organo-clay containing 9.4% of organic surfactant.

The organoclay was freeze-dried and characterized by X-ray spectroscopy. The diffractogram of the sample shows that the d_{001} spacing is not altered when compared to that of the clay in the Na^+ homo-ionic form, indicating that the surfactant did not migrate into the interlamelar spaces of the clay.

Preparation of Probe/Organoclay Samples

1 μL of a pyrene solution (1×10^{-3} M in benzene) was added to a pre-weighted amount of the organoclay (0.20 g), corresponding to 10^{-9} moles of the probe in 0.02 g of the organic layer, i.e. a 5×10^{-5} M concentration. Milliliter-aliquots (10 to 100 μL) from a stock solution of perylene (1.25×10^{-3} M in benzene) were added as quickly as possible, under stirring, to the pyrene-organoclay sample. The largest volume of these

Table 1. Properties of Laponite B.

Clay	Type	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	Fe_2O_3 (%)	area (m^2/g)	CEC (meq/100 g clay)
Laponite B	Synthetic hect.	55.6	0.08	25.1	0.04	360	73.3

additions was 150 μL to prevent any dilution effect, so as to obtain concentrations from 0.6 to 6 × 10^{-3} M of the quencher in the adsorbed organic phase. After stirring for 24 h, the slurry was kept under N_2 flow until total evaporation of the solvent, and stored under vacuum.

Results and Discussion

The organo-clay used in this work has practically all of the surfactant adsorbed on the external surface of the tactoids, as the rapid addition of the surfactant and prompt flocculation of the suspension does not allow the migration to the interlamellar region. This flocculation is due to the instantaneous compensation of the negative charges of the clay particles by the positively charged surfactant, cancelling the hydrophilicity of the clay. Therefore, one of the interesting features of the organoclay prepared by this procedure is that it cannot be dissolved or dispersed in water, due to the fact that all the particles are literally covered by surfactant which makes the clay very hydrophobic.

The same type of organoclays, with the surfactant on the external surfaces, is observed for clays with narrower interlamellar spaces (like ST$x-1$) which prevent the migration to these regions, or when using long chain surfactants (C_{16}–C_{18}). On the other hand, the use of C_{12}- or shorter chain surfactants facilitates their incorporation. Furthermore, when the addition of the surfactant to the clay is performed slowly there is sufficient time for the initially formed surfactant clusters on the external surface of the tactoids to deaggregate and migrate into the interlamellar spaces. In this case, the whole process is similar to that observed for the interactions of clays with smaller molecules, as for instance, dyes (Ferreira et al., to be published; Cione et al., 1998; Gessner et al., 1994; Neumann et al., 1996).

The hydrocarbons used as probes are adsorbed preferentially in the organic phase of the clay and no adsorption is observed on clays without surfactant, even when the clay was pre-activated in vacuum at 200°C to remove the water molecules from the surface.

Pyrene on C_{18}-Laponite

Figure 1 shows the emission spectra of pyrene in the presence of different amounts of perylene. As can be seen from the spectrum in the absence of acceptor, there is a rather large tail towards the visible region, which may be assigned to the excimer emission. This spectrum is qualitatively similar to those found for the adsorption of pyrene on bare Laponite (Liu and Thomas, 1991). Nevertheless, the ratio of the intensities of peaks I_1/I_3 is significantly higher than that found in that work. Whereas on inactivated bare Laponite the ratio was found to be around 1.0, when the surfactant covered Laponite is used this ratio is about 1.25. This indicates that the probe is placed in an environment very similar to that found in surfactant micelles (1.2–1.4) (Kalyanasundaram, 1987).

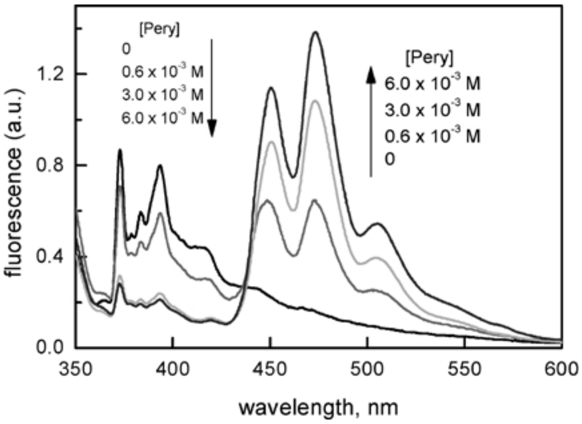


Figure 1. Steady state fluorescence spectra of pyrene on C18-Laponite (5 × 10^{-5} M in the surfactant layer) in the presence of increasing concentrations of perylene (0.6 × 10^{-3}, 3.0 × 10^{-3} and 6.0 × 10^{-3} M in the surfactant layer).

The fluorescence decay of pure pyrene adsorbed on the organic clay was measured by single photon counting, and the decay curve could reasonably be recovered with a bi-exponential approximation. The lifetimes obtained were 1.33 and 6.1 ns, with B-values of 0.054 and 0.010, respectively, and a χ^2 of 1.084. Although there might be a large number of different sites in which the probe could be located, it is usually accepted that a good approximation can be obtained assuming a bi-exponential decay and dividing those sites in two classes (Ramamurthy, 1994; Tiera et al., 1994).

On the other hand, the rather low lifetimes for pyrene can be traced to some residual concentration of the bromine counter-ions originated from the surfactant salt. Due to the wavelengths used for excitation and emission detection, it doesn't seem that the excimer should have a significant contribution to the emission in that region.

Energy Transfer from Excited Pyrene to Perylene Adsorbed on C_{18}-Laponite

Energy-transfer between an excited donor and an acceptor can occur by various mechanisms. Processes with rate constants larger than the diffusional limit occur, according to Förster by a mechanism that involves dipole-dipole interactions between the species. Therefore, the corresponding rate constant will be inversely proportional to the sixth power of the distance between both molecules (Förster, 1959; Lakowicz, 1999)

$$k_{ET} = \frac{9000 \ln 10}{128\pi^6 N} \cdot \frac{\kappa^2 \phi_D}{n^4 \tau_D R^6} \cdot J \tag{1}$$

where N is the Avogadro constant, κ^2 is a factor related to the relative orientation of the dipole moments, ϕ_D is the donor fluorescence quantum yield in the absence of acceptor, τ_D is the donor fluorescence lifetime in the absence of acceptor, n is the refraction index of the medium, R is the distance between the donor and the acceptor, and J is the overlap integral between the donor normalized emission spectrum F_D and the aceptor normalized absorption spectrum ε_A, both in wavenumber units

$$J = \int_0^\infty F_D(\bar{\nu})\varepsilon_A(\bar{\nu})\frac{d\bar{\nu}}{(\bar{\nu})^4} \tag{2}$$

From that equation a critical transfer distance, R_o, the Förster radius, can be defined as the distance at which the rate constant for the deactivation of the excited donor by energy-transfer is equal to the decay rate constant

$$R_o^6 = \frac{9000 \ln(10)\phi_D}{128\pi^6 N n^4} J \tag{3}$$

Using this expression in Eq. (1) the dependence of the rate constant with the distance will be

$$k(r) = \frac{3}{2}\kappa^2 \left(\frac{R_o}{r}\right)^6 \tau_o^{-1} \tag{4}$$

The Förster radius can be estimated using data obtained from sources not involving quenching experiments, i.e. donor lifetimes, quantum yields and spectra from fluorescence measurements and acceptor spectra from spectroscopic data. The refraction indexes are taken from appropriate tables and the factor κ^2 can be calculated.

It can be seen from Fig. 1 that the fluorescence emission of pyrene is efficiently quenched by perylene. A treatment frequently used to determine the quenching efficiency is base on the Perrin approximation, which relates the rate constants in the presence and absence of quencher with the distance between the excited donor and the quencher molecules.

In this case, the critical quenching distance will be (Förster, 1959; Lakowicz, 1999)

$$R_o = \left[\frac{3 \times 10^{27}}{4\pi N C_o}\right]^{1/3} \tag{5}$$

where C_o corresponds to the quencher concentration at which the quenching rate is equal to the decay rate. A direct and simple application of this expression using the $1/C_o$ value ($= 381$ L·mol^{-1}) determined from the initial slope of the Perrin plot shown in Fig. 2 gives a value of R_o of 53.3 Å.

On the other hand, the same distance can be calculated theoretically using Eq. (3) with data obtained from other experiments and determining the overlap integral J between the pyrene absorption and the perylene emission spectra. The emission quantum yield of pyrene adsorbed on the organoclay (ϕ_D) was taken as 0.4, similar to the value determined in solid silica (Rueten and Thomas, 1998). The value of κ^2 for solid samples is 0.446 (Kalyanasundaram, 1987). The refraction index for the medium is assumed to be 1.45, which corresponds to a long chain hydrocarbon, somehow similar of what can be expected for both reagents immersed in the surfactant layer.

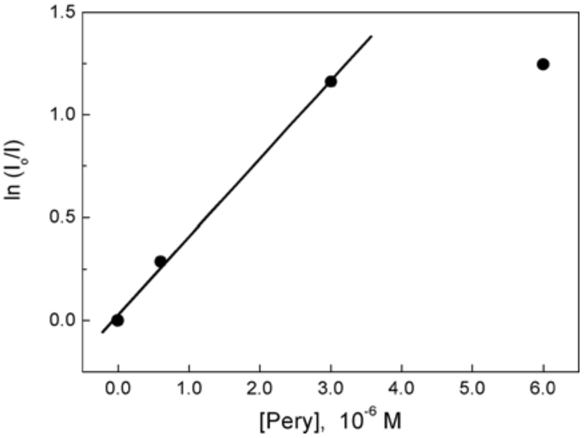


Figure 2. Perrin plot for the quenching of pyrene by perylene in the C18-Laponite organoclay.

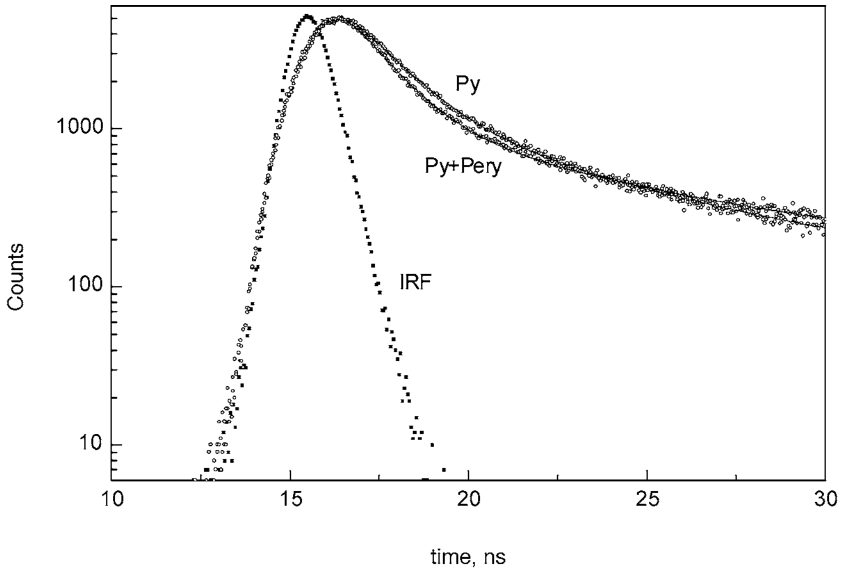


Figure 3. Pyrene (5×10^{-5} M) emission decay in the absence of quencher (Py), and in the presence of perylene 6.0×10^{-3} M (Py + Pery). Full lines represent the fitting curves.

Using the values described above together with the overlap integral, calculated as 2.20×10^{-12}, a value of 53 ± 7 Å is obtained for the Förster radius, in good agreement with that determined experimentally from the Perrin approach.

These values for the interaction radius confirm that the hydrocarbons will be placed in a homogeneous medium formed by the hydrophobic part of the surfactants, which will be present as a defined layer on the surfaces. This distance also confirms that the mechanism is of Förster type, as no need of physical contact between the species is necessary. Energy transfer between pyrene and perylene was also used studied in other similar matrices like zeolites (Iu and Thomas, 1990; Liu et al., 1989) and silica (Marro and Thomas, 1993). In zeolites the Förster radii were determined to be 38–40 Å, but the energy transfer process could be altered by modifications of the microenvironment where the probes are adsorbed, like hydration/dehydration. For similar experiments on silica surfaces, the diffusion of the hydrocarbon molecules was studied by kinetic methods, and the results indicated that the probe molecules were adsorbed on preferential sites of the silica surface, so that the critical radius for energy transfer depended on the amount of silanol groups on the surface. This property could be controlled by heating the silica (Marro and Thomas, 1993).

The decay of the pyrene emission in the presence of perylene (shown in Fig. 3) can also be approximated by a bi-exponential curve, with values of 1.07 and 6.1 ns, and weight factors of 0.058 and 0.008, respectively. The critical distance for the energy transfer in this system, can also be calculated assuming Förster quenching (Gem program available from Edinburg) by adjusting the expression to the experimental curves

$$Y(t) = A + B_1 \exp\left[\left(\frac{-t}{\tau_1}\right) - 2\gamma\left(\frac{t}{\tau}\right)^{1/2}\right] \tag{6}$$

$$2\gamma = \frac{4}{3} g \pi^{3/2} n_a R_o^3 \tag{7}$$

where n_a is the density of acceptor molecules (2.17×10^{18} molecules/cm^3) and g is a weight factor. The best adjustment was obtained for a γ-value of 0.004 ($\chi^2 = 1.370$), rendering a critical energy transfer distance of 13 ± 3 Å for the pyrene-perylene pair. This value is certainly too low for this system. A serious uncertainty about this distance can arise due to the large χ^2-value, as well as to the fact that the calculation procedure assumes a fluid isotropic solution.

Conclusions

Energy transfer experiments carried out in solid matrices yield information about the microenvironment in which the pair of probes are adsorbed or dissolved. The organoclay prepared from Laponite and C18 using the procedure indicated in this paper contains all the organic phase adsorbed on the external surface of the tactoids, forming a homogeneous surfactant layer, in which the hydrocarbons are dissolved. This is confirmed by the I_1/I_3 value of 1.25 for the fine structure of the pyrene emission.

The experimental critical radii for the energy transfer between pyrene and perylene was 53.3 Å was calculated using the Perrin approach, in excellent agreement with the calculated value of 53 ± 7 Å. These values are also within the range known for the same pair in other solid clay systems.

These results suggest that it is possible to design organoclays with specific characteristics by relative simple experimental control.

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