The excimer emission of aromatic hydrocarbons on clays

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Abstract

The emission of some aromatic hydrocarbons on the surface of hectorite (Laponite and SHCa-1) and montmorillonite (SWy-1, Volclay, STx-1 and Syn-1) clays was studied. *p*-Terphenyl, biphenyl and naphthalene, when adsorbed on clays showed excimer emissions, as well as the well-known molecular fluorescence bands, but on SWy-1 and Volclay the emissions were relatively weak. As the loading was increased, the excimer emission tends to dominate the emission spectra, particularly for the montmorillonites STx-1 and Syn-1. Emission due to microcrystals on the clay surface was also detected at larger loadings. No excimer emissions were detected for *m*-terphenyl and 1,1′-binaphthyl even at the larger loadings used. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Clay materials have interesting properties such as very high surface areas available for interaction with organic molecules, including internal (interlamelar) spaces in which these molecules can be intercalated. Therefore, clays have been extensively used in many applications such as catalysts for organic reactions [1,2], adsorbents in purification processes [3] and additives in drilling fluids for the petroleum industry [4,5]. These materials are an interesting medium for chemical reactions and have been extensively studied by researchers in many areas employing different techniques [6]. Among them, photochemical techniques have been used successfully and information about the microscopic domains present in clays were obtained studying the photoprocesses of molecules adsorbed on the clay surface [7–9].

A large number of studies involving aromatic molecules and heterogeneous systems (including zeolites, clays, alumina, etc.) has been reported independently by Ramamurthy and Thomas. Ramamurthy et al. discussed the interactions of molecules such as pyrene, naphthalene and phenanthrene with NaY zeolites and the heavy atom effects of different cations present on clays [10–14]. Thomas et al. used pyrene as a photochemical probe to investigate the surface properties of clays (Laponite) and alumina [7,15–23]. Hashimoto studied the interactions of hydrocarbons on a NaX zeolite, and was able to detect the emission of anthracene excimers [24]. Systems with clays as support were not studied so frequently, especially for dry systems.

In this paper we report a study of the emission of some aromatic hydrocarbons on solid clays. Excimer emissions for *p*-terphenyl and biphenyl (not found in homogeneous solutions) are reported for the first time. The photophysical behaviour of the adsorbed hydrocarbons is discussed in terms of the properties of the clays used.

2. Experimental

2.1. Chemicals

Natural and synthetic montmorillonites (SWy-1, STx-1, Syn-1) and hectorite (SHCa-1) were obtained from the Source Clays, Clay Minerals Society, University of Missouri, Columbia, MO. Laponite B was from Laporte, UK. These clays were purified as described in an earlier work by Gessner et al. [25]. The aromatic hydrocarbons were *p*-terphenyl (Aldrich, scintillation grade), pyrene (Aldrich, re-crystallized twice from methanol), 1, 1′-binaphthyl (Kodak, re-crystallized twice from hexane), naphthalene (Merck, used as received), and biphenyl (Merck, re-crystallized from ethanol). Solution of the probes were prepared in hexane (Mallinckrodt, HPLC grade).

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2.2. Preparation of probe/clay samples

The samples were prepared by previously dissolving the required amount of the probe in ca. 50 ml of hexane and adding this solution to a pre-weighed amount of clay ($\sim$0.25 g). After stirring for 24 h, the slurry was kept under N_2 flow until total evaporation of the solvent and stored under vacuum. In order to maximize the area available on the clay surfaces for the probe molecules, freeze dried clay was used in all experiments.

2.3. Instruments

Emission spectra were recorded on a Hitachi F-4500 Spectrofluorimeter, with a front face accessory, using 1.0 cm quartz cuvettes. All measurements were performed at room temperature ($25 \pm 1°C$). Fluorescence lifetimes were measured by the time-correlated single-photon counting method using an Edinburgh CD-900 instrument. The fluorescence decay profiles were analysed with a non-linear least-squares iterative re-convolution method.

3. Results

Fig. 1 shows the emission spectra of *p*-terphenyl on different clays at low loading (1% w/w). These spectra are quite different from those obtained in organic solvents. In solution the emission bands are found in the 310–360 nm region, with intense bands appearing around 320–340 nm. When the hydrocarbon is adsorbed on clays the main feature of the spectra is the presence of a broad emission around
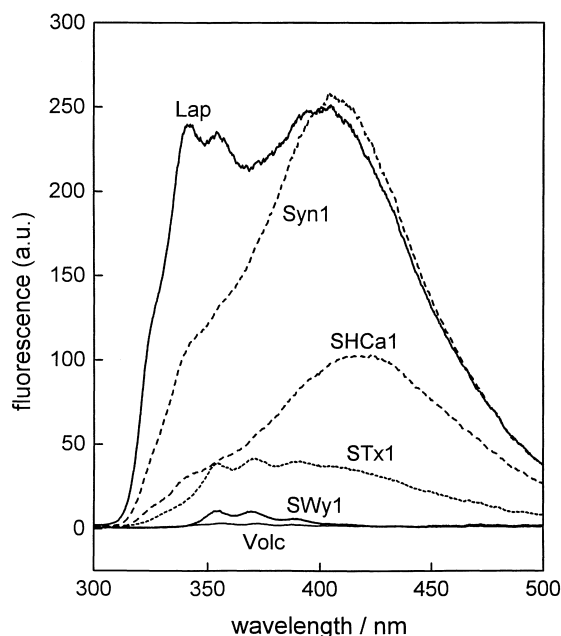
Fig. 1. Fluorescence emission spectra of *p*-terphenyl on Laponite, SHCa-1, STx-1, SWy-1, Syn-1 and Volclay (1% w/w, λ_{exe} = 280 nm).
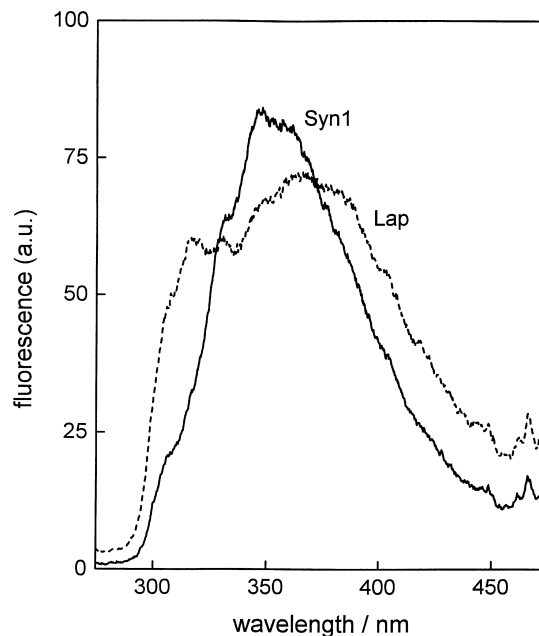
Fig. 2. Fluorescence emission spectra of biphenyl on Laponite and Syn-1 (1% w/w, λ_{exe} = 280 nm).

410 nm. For Laponite and Syn-1, an intense emission band is also observed at shorter wavelengths, similar to those in solution. The overall emission intensity depends on the particular clay, and on the SWy-1 and Volclay montmorillonites these emissions are severely quenched.

The same trend is observed for the emission of biphenyl on these clays. Fig. 2 shows the spectra of biphenyl on Laponite and Syn-1. On Laponite two strong emission bands are observed in the 313 and 363 nm regions. When the probe is adsorbed/deposited on the other clays (e.g., Syn-1), the emission spectra is dominated by a broad emission band around 350–365 mm. As observed for *p*-terphenyl, the emission on the SWy-1 and Volclay clays is quite weak.

Pyrene (1% w/w) was used in order to gain more information on the behaviour of these probes on the clays. The emission characteristics of this molecule are well known, and this compound has been extensively used as a photochemical probe in many systems [20–22]. The emission characteristics of pyrene on the clay systems under the same conditions as described above are similar to those of *p*-terphenyl and biphenyl. For the synthetic clays Laponite and Syn-1 (Fig. 3), an intense emission was detected around 480 nm, corresponding to the well-known excimer emission [26–28]. When on the natural hectorite SHCa-1, the monomeric emission is barely seen, whereas on STx-1 only the excimer emission is detected. Again, on SWy-1 and Volclay only very weak emissions were detected.

3.1. Effect of loading

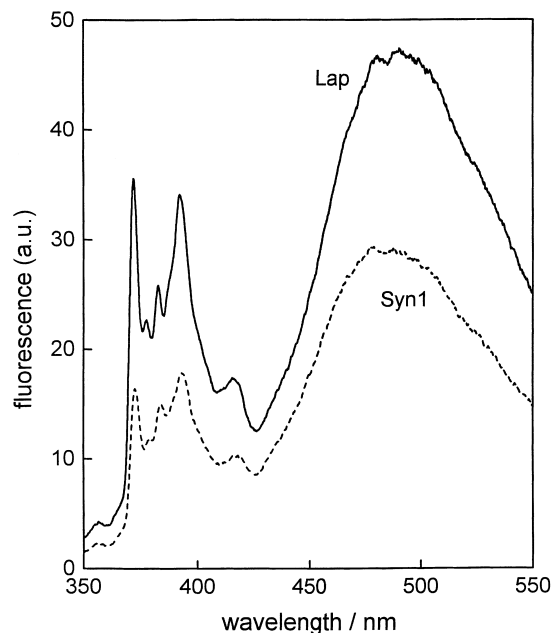Fig. 4 shows the emission spectra for *p*-terphenyl on Laponite at different loadings. The emission of *p*-terphenyl

Fig. 3. Fluorescence emission spectra of pyrene of Laponite and Syn-1 (1% w/w, $\lambda_{exe} = 340$ nm).

crystals is also shown for comparison. In the case of Laponite, for low loadings (around 0.2%) the spectrum shows an emission band around 340 nm assigned to p-terphenyl molecules, and a shoulder in the 410 nm region. As the loading increases, the emission around 340 nm becomes progressively weaker and the intensities around 410 nm increases, eventually dominating the spectra. At the same time, the overall emission is steadily quenched as the
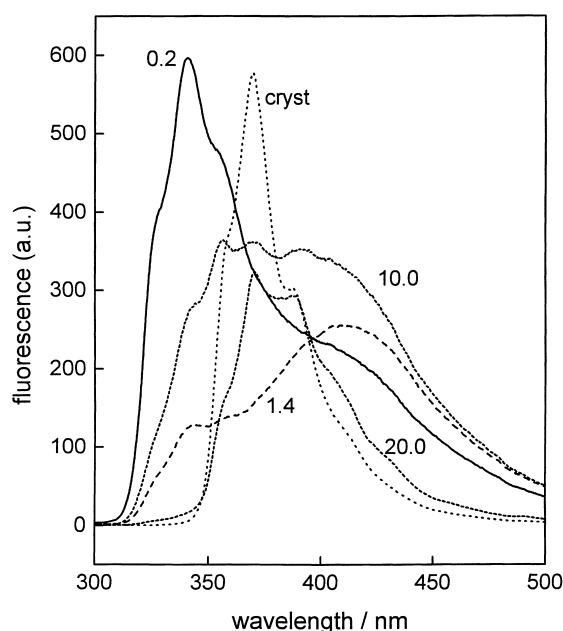
loading increases because of the interaction with other adsorbed molecules. As can be seen, the emission due to p-terphenyl crystals is centered at lower wavelengths (∼340 nm), and is only observed at loadings of 10% w/w or higher. When the STx-1 montmorillonite is used, the same trend is observed. As the loading increases the emission around 410 nm tends to dominate the spectra, although at much smaller loadings than those for Laponite. Similarly, in STx-1 the emission due to p-terphenyl crystals is also observed at considerably lower loadings.

The results obtained for biphenyl and pyrene are similar to those for p-terphenyl. As the loading increases, the emission of the probes at shorter wavelengths (biphenyl around 313 nm and pyrene around 340 nm) is progressively replaced by the broader emissions at longer wavelengths (363 and 470 nm for biphenyl and pyrene, respectively). This effect also depends on the clay used, being always more intense on STx-1 than on Laponite. Since the emissions at longer wavelengths are not due to crystals, and considering the similarities with the spectral behaviour of pyrene, the emissions at longer wavelengths for p-terphenyl and biphenyl can also be assigned to excimer emissions.

Fig. 5 shows the excitation spectra of p-terphenyl on Laponite. For low (0.5% w/w) and high (7% w/w) loadings. When monitoring the emission at 340 nm (corresponding to the monomolecular form of the probe) a broad peak is observed around 290 nm, and no significant differences were observed between the spectra of the systems with low and high loadings. On the other hand, when monitoring at 410 nm (corresponding to the excimer emission), the system with high loading showed an additional band at

Fig. 4. Fluorescence emission spectra of p-terphenyl on Laponite at different loadings (0.2, 1.4, 10.0 and 20.0% w/w) and of p-terphenyl crystals ($\lambda_{exe} = 280$ nm).
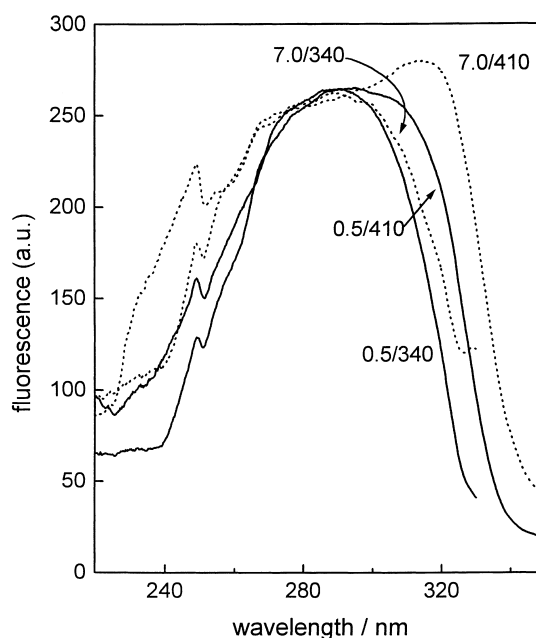

Fig. 5. Fluorescence excitation spectra of p-terphenyl on Laponite at loadings of 0.5% and 7.0% w/w, monitored at 340 nm and 410 nm. The spectra are normalized at 290 nm.

Table 1
Lifetimes of the emission decay of *p*-terphenyl on Laponite

λ_{det}	340 nm	410 nm			
Loading w/w	τ_1 ns	τ_1 ns	τ_2 ns	b_1	b_2
0.05	1.04	1.34	21.5	0.98	0.17
0.2	0.96	1.63	20.8	0.77	0.23
0.8	0.89	1.89	18.8	0.66	0.34
7.0	0.75	2.46	20.5	0.30	0.69

315 nm. This suggests interactions between the probe molecules in the ground state, so that the entity responsible for the excimer emission is already present before excitation. Thus, rather than a excimer emission what is observed is the emission of the excited dimer. Similar considerations for pyrene on zeolites were made by Ramamurthy [10,11].

3.2. Lifetimes

The decay times of *p*-terphenyl on Laponite are shown in Table 1. The decay at 340 nm is mainly single exponential, with values around 1.0–0.7 ns, depending on the loading of the probe. Higher loadings reduce the lifetime, probably due to quenching by vicinal probe molecules. On the other hand, the decay at 410 nm could be reproduced with a double exponential, proving the existence of (at least) two emitting species at this wavelength. The shorter lifetime varies from 1.3 to 2.5 ns with the increase of the loading on the clay, whereas the second lifetime remains basically constant around 20 ns. The relative weights of both lifetimes are indicated in the table by b_1 and b_2, show an increase of the 20 ns component at higher loadings. The latter can be ascribed to the excimer (dimer) emission, only observable at the longer wavelength. The short lifetime, obtained when measuring at both wavelength should be the monomer emission. Its increase with increasing loadings are due to the fact that only a biexponential has been used, not taking into account the eventual emissions of species with longer lifetime, like higher aggregates and even microcrystals at the higher loadings. Longer lifetimes for adsorbed aggregates have already been observed for pyrene on NaY faujasite [7–9], contrary to what happens in solution.

4. Discussion

The emission intensities of the probes on Laponite were always higher than on the other clays. Laponite is a synthetic hectorite, and the presence of quenching elements or impurities in its structure is not as common as in the natural clays. Among the clay used the Wyoming montmorillonites SWy-1 and Volclay have the higher iron content [25]. Therefore, relatively weak emissions were detected for the probes when on these clays.

Also when the aromatic molecules are deposited/adsorbed on these iron-rich clays, the development of colour is readily

observed, and assigned to radical cations stabilized by the clay surface [29–31], formed by the interaction between the excited organic molecules and the iron ions present in the clay. In fact, laser photolysis experiments have shown that radical cations of these probes on clays are readily formed after excitation [23]. Transition metals present as impurities in the natural clays, will improve the catalytic effect of these minerals and promote reactions of organic compounds in the ground and excited states [25].

The particle size also exerts a strong effect on the photophysics of the probes, as observed comparing the emission intensity of *p*-terphenyl on Laponite and STx-1. The fluorescence spectra of the excimer band of *p*-terphenyl on STx-1 resembles the spectra on Laponite, but at considerable smaller loadings. The particles of Laponite are smaller than those of STx-1, so that for the same loading (w/w), the surface concentration of the probe on STx-1 will be considerably higher than on Laponite, favouring the formation of dimers.

It should be noted that the excimers of compounds such as pyrene are easily observed in homogeneous solutions, but for molecules like *p*-terphenyl and biphenyl the excimer emissions are not usually observed, even at high concentrations (up to 10^{-3} M, see [32]). The phenyl rings in *p*-terphenyl and in biphenyl are not in the same plane but twisted, hindering the interaction between the ground and excited molecules to form excimers in solution. When on the clay, the surface will act promoting the *p*-terphenyl molecules even in the ground state, as revealed by the difference in the excitation spectra of *p*-terphenyl on the clay at increasing loadings.

Interestingly, no excimer emissions was detected for *m*-terphenyl on the same clays, even for the highest loadings used. The interactions between *m*-terphenyl molecules should be more difficult compared to *p*-terphenyl as the ring in the *meta*-position makes the interaction between the *m*-terphenyl molecules more difficult. In this molecule the three rings are not in the same plane even in the excited state, hindering the interaction of *m*-terphenyl molecules to form excimers. A similar behaviour was observed for 1,1′-binaphthyl on the clays, for which no excimer emission was observed, even for loadings as high as 20%. The two naphthalene-like moieties in the binaphthyl molecule are not in the same plane, being twisted when in the ground state, but assuming a more planar conformation in the excited state in homogeneous solution. The same is observed when the probe is on the clay surface. The fluorescence spectra is similar to that detected in solution, and different from the fluorescence spectra of naphthalene, indicating that the clay surface did not hinder the movement of the naphthalene moieties towards a more planar confirmation in the excited state. On the other hand, excimer emission was readily detected for naphthalene on Laponite and on SYn-1, as well as on the Na13X zeolite [32].

The characteristic fluorescence of *p*-terphenyl was detected for this compound on NaX zeolite. While increas-

ing the loading the emission due to crystals starts to appear and no excimer emission is detected.

5. Conclusions

When organic hydrocarbons such as *p*-terphenyl, binaphthyl, naphthalene and pyrene are deposited on the surfaces of clays like Laponite, STx-1 and Syn-1 it is possible to observe emissions from the probe, and as the loading increases, an excimer emission similar to that observed for pyrene is also detected. Further increase in loading leads to emissions due to microcrystals on the clay surface. When the same molecules are deposited on Wyoming montmorillonites only very weak emission is detected, probably due the relative high Fe content. These clays are more prompt to form coloured compounds due to oxidation/reduction reactions forming stable radical ions on the clay surface, as compared with zeolites.

Compared to Laponite, the excimer emissions from the probes were detected at considerably lower loading in the STx-1 montmorillonite. This is due to the higher surface area of Laponite, leading to higher surface concentrations in the STx-1.

Excimer emissions were not detected for molecules like *m*-terphenyl and 1,1′-binaphthyl, due to the non planarity leading to a more effective steric hindrance of these molecules in the ground state.

Although the long wavelength emissions at high loading correspond to the excimer spectra, it has to be pointed out that in this case the emission actually originates from the excitation of dimers already present in the ground state.

Acknowledgements

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