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Letter

Selective adsorption of nitro-substituted aromatics and accelerated hydrolysis of 4-nitrophenyl acetate on carbon surfaces

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Nitrobenzene, 4-nitrotoluene and 4-nitrophenyl acetate are selectively adsorbed from aqueous 1% sodium dodecyl sulfate solutions onto aligned, randomly oriented and oxidised carbon nanotubes, as well as graphite and C_{60} fullerene. The rate of hydrolysis of 4-nitrophenyl acetate to 4-nitrophenolate is modestly accelerated through this process. Selective adsorption requires the presence of the surfactant and the hydrolysis of *p*NPA is accelerated only by a carbon surface that is graphitic in nature.

Graphite[1] is a crystalline form of carbon that consists of planar layers of atoms, known to adsorb surfactants[2] and other organic compounds[3] from aqueous solutions. In the last decade, two new forms of carbon, the fullerenes and carbon nanotubes, have been discovered.[4] Carbon nanotubes consist of graphite planes forming the walls of nanometre diameter cylinders and have attracted much attention because of their potential applications.[5] Although they are usually prepared in a random and entangled manner, ourselves[6] and others[7] have recently prepared them aligned orthogonally to a surface. Only a limited number of studies of the adsorption characteristics of fullerenes[8] and carbon nanotubes[9] have been reported and, to our knowledge, no report on the adsorption of organic compounds from aqueous solutions onto carbon nanotubes has appeared. In the present study, therefore, the adsorption of various organic compounds from their aqueous surfactant solutions onto a wide range of graphitised carbon surfaces was investigated.

Since it has been reported that nitrobenzene and its derivatives are adsorbed from aqueous solution onto graphite,[10] we chose to investigate the adsorption characteristics of predominantly nitro-substituted aromatic compounds (these are listed in ref. 11). This class of compound also absorbs strongly in the UV region, which facilitates monitoring of the solutions by UV-visible spectroscopy. Each compound was solubilised into a dilute anionic surfactant solution containing 1% (35 mM) sodium dodecyl sulfate (SDS) in water. The surfactant was used to permit wetting of the carbon surfaces and to solubilise the organic compounds. The solutions were then exposed to aligned,[6] randomly oriented[12] and oxidised carbon nanotubes[13] as well as graphite powder and C_{60} fullerene. Of the systems investigated,[11] only the solutions of nitrobenzene, 4-nitrotoluene and 4-nitrophenyl acetate (*p*NPA) showed substantial changes in absorption intensity over time. In each case, a decrease in the absorption at the absorbance maximum (λ_{max}) was seen. The spectra of solutions of nitrobenzene and 4-nitrotoluene exposed to aligned carbon nanotubes are shown in Fig. 1. Analogous spectral changes were also observed when solutions of nitrobenzene and 4-nitrotoluene were exposed to the aforementioned other graphitised carbon forms. A small decrease in the absorption (*ca.* 0.1 units) at λ_{max} was also seen for a solution of 2-nitrotoluene exposed to each carbon form over a period of 14 days. The decrease in absorption over time is indicative of a reduction in the concentration of the aromatic compound in solution and, since no chemical reaction was detected, presumably adsorption onto the carbon surface had occurred. This was supported by X-ray photoelectron spectroscopy (XPS) measurements, which revealed that aligned carbon nanotube samples exposed to solutions of nitrobenzene or 4-nitrotoluene showed a characteristic peak in the nitrogen region of the spectrum, attributable to the presence of nitro groups on the surface. The quantity adsorbed onto the surface area (1 cm^2) of these nanotube samples was calculated to be 0.02 mg of nitrobenzene or 4-nitrotoluene over 7 days.[14] Where possible, solutions of the

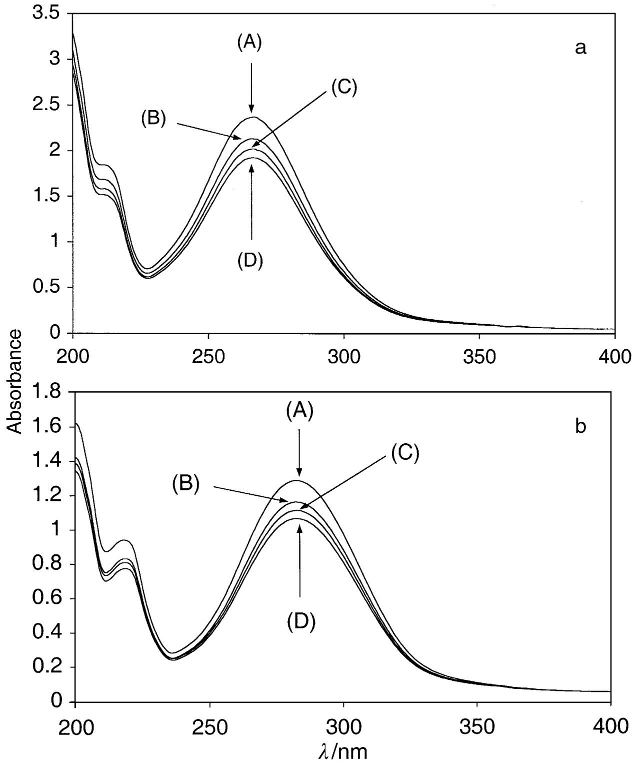

Fig. 1 Spectra of (a) 1.62×10^{-4} M nitrobenzene and (b) 1.46×10^{-4} M 4-nitrotoluene aq. 1% SDS solutions (5 ml) exposed to aligned carbon nanotubes (sample area *ca.* 1 cm^2) at 298 K. Spectra recorded after (A) 0, (B) 3, (C) 5 and (D) 7 days.

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nitro-substituted aromatic compounds listed in ref. 11 (and also nitrobenzene, 4-nitrotoluene and *p*NPA) were prepared in the absence of SDS and exposed to the carbon surfaces. In all these cases, a decrease in the absorption at λ_{max} was observed.

The selective adsorption from the surfactant solutions is presumably attributable to SDS, which forms micelles in an aqueous solution above the critical micelle concentration of 8.1 mM.[15] This surfactant also aggregates at solid–solution interfaces and is reported to assemble on the surface of graphite in an organised periodic structure consisting of long parallel flattened tubes (termed 'hemimicelles').[16] Since it is known that SDS complexes *p*NPA specifically at the micelle–solution interface,[17] it can be postulated that *p*NPA complexed with a hemimicelle is in a favourable environment to be adsorbed because of its close proximity to the graphitised carbon surface. Nitrobenzene and 4-nitrotoluene may behave and be adsorbed in a similar fashion. The compounds listed in ref. 11 are perhaps complexed with SDS in a different manner (for example, sequestered within the hydrophobic core of a micelle/hemimicelle) and are thus unable to be adsorbed.

We were intrigued to discover that *p*NPA not only adsorbed onto the carbon surfaces, but this also accelerated its rate of hydrolysis. The changes in the UV-vis spectrum in the presence of aligned carbon nanotubes are shown in Fig. 2(a). With time, the absorbance of *p*NPA, ($\lambda_{max} = 272$ nm) decreased and that of its hydrolysis product, 4-nitrophenolate ($\lambda_{max} = 401$ nm), increased. Hydrolysis was also observed in the absence of a carbon surface, but the rate was much slower [Fig. 2(b)]. Moreover, only a graphitised carbon form such as that used in this study accelerated the rate of hydrolysis. With amorphous activated carbon, only adsorption of *p*NPA was observed. An insight into the mechanism of hydrolysis in the presence of graphitised carbon is provided by the observation that the absorption of 4-nitrophenolate [$\lambda_{max} = 401$ nm, Fig. 2(a)] increased to a greater extent between 7 and 14 days than between 0 and 7 days. The hydrolysis is therefore not a pseudo-first order process and can be assumed to be initiated by slow adsorption onto the carbon nanotube surface. This adsorption process manifests itself as an inexact isosbestic point at *ca.* 305 nm, which is in contrast to the precise isosbestic point observed for spectra from the control experiment [Fig. 2(b)]. The control experiment shows that accelerated hydrolysis of *p*NPA is not due to simple micellar catalysis, there is a possibility that the hemimicelles on the carbon surfaces may have different properties that induce the catalysis.

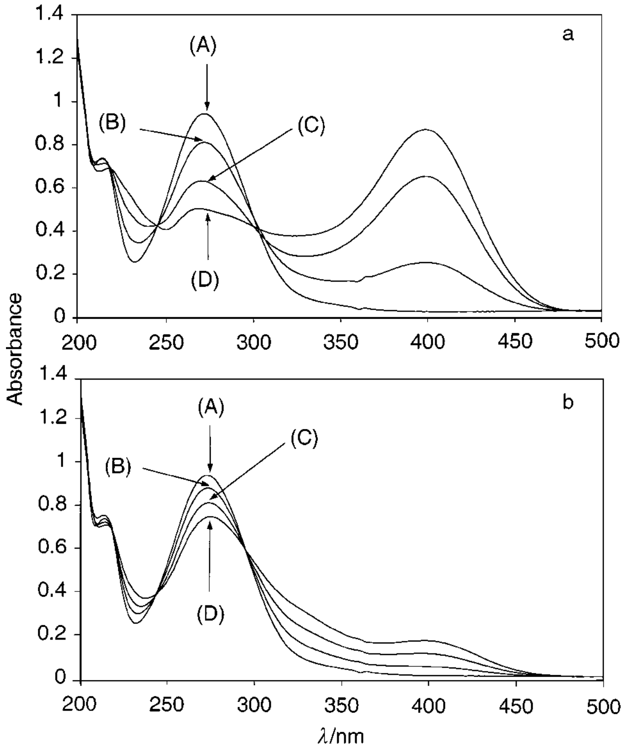

Fig. 2 UV-vis spectra showing hydrolysis of *p*NPA (5.0×10^{-5} M) in an aq. 1% SDS solution (5 ml) at 298 K (a) with and (b) without exposure to aligned carbon nanotubes (sample area *ca.* 1 cm^2) at 298 K. Spectra recorded after (A) 0, (B) 7, (C) 14 and (D) 21 days.

Experimental

Aligned carbon nanotubes were prepared on quartz plates according to the method described previously.[6] Oxidised nanotubes were obtained by treatment of aligned nanotubes, scraped from the quartz surface, with boiling nitric acid.[13] Optically transparent solutions of oxidised nanotubes were prepared by their dispersion in an aqueous 1% SDS solution (1 mg ml^{-1}). Randomly oriented carbon nanotubes ('buckytubes'), graphite powder (1–2 micron in diameter) and activated carbon were purchased from Aldrich Chemical Co. C_{60} fullerene was supplied by Yin Han Hi-Tech C_{60} Co., Wuhan University, China. SDS was purchased from Merck Chemical Co. All of the chemicals from commercial sources were used as received. De-ionised water was distilled and was of pH 6.0. UV-vis spectra were recorded on a Hewlett Packard HP 8453 spectrophotometer. XPS analyses were performed on a Kratos Analytical spectrometer using monochromatic Al-Kα radiation at a power of 200 W. Compounds investigated were dissolved in an aqueous 1% SDS solution (2 mg per 100 ml) by sonicating for 1 h. In a typical experiment, a solution of the compound (5 ml) was added to a vial containing the carbon sample (5 mg for buckytube, graphite or C_{60} fullerene powders) and then sealed under an atmosphere of nitrogen. An aliquot (3 ml) was removed and added to a quartz cell (1 cm pathlength), and the UV-vis spectrum was recorded every 24 h for a period of 7 days unless otherwise stated. The hydrolysis of a solution (5 ml) of *p*NPA (5×10^{-5} M) containing a carbon sample was monitored spectrophotometrically and the increase in absorbance at 401 nm, due to 4-nitrophenolate liberation, was recorded each day for a period of 21 days (*i.e.*, monitored through to at least 90% completion).

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Notes and references

1 D. B. Fischback, in *Chemistry and Physics of Carbon*, ed. P. L. Walker, Marcel Dekker, Inc., New York, 1971, vol. 7.
2 J. H. Clint, *Surfactant Aggregation*, Chapman and Hall, New York, 1992, ch. 9.
3 Z. Király, I. Dékány, E. Klumpp, H. Lewandowski, H. D. Narres and M. J. Schwuger, *Langmuir*, 1996, **12**, 423, and references cited therein.
4 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, London, 1996.
5 T. Ebbesen, *Carbon Nanotubes*, CRC Press, Boca Raton, FL, USA, 1997.
6 (*a*) S. Huang, L. Dai and A. W. H. Mau, *J. Phys. Chem. B*, 1999, **103**, 4223; (*b*) L. Dai and A. W. H. Mau, *J. Phys. Chem. B*, 2000, **104**, 1891 and references cited therein.
7 (*a*) C. N. R. Rao, R. Sen, B. C. Satishkumar and A. Govindaraj, *Chem. Commun.*, 1998, 1525; (*b*) Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegel and P. N. Provencio, *Science*, 1998, **282**, 1005; (*c*) S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell and H. Dai, *Science*, 1999, **283**, 512.
8 (*a*) M. H. Abraham, C. M. Du, J. W. Grate, R. A. McGill and W. J. Shuely, *J. Chem. Soc., Chem. Commun.*, 1993, 1863; (*b*) V. Yu.

Gusev, S. Ruetsch, L. A. Popeko and I. E. Popeko, *J. Phys. Chem. B*, 1999, **103**, 6498 and references cited therein.

9 (*a*) S. A. Curran, P. M. Ajayan, W. J. Blau, D. L. Carroll, J. N. Coleman, A. B. Dalton, A. P. Davey, A. Drury, B. McCarthy, S. Maier and A. Strevens, *Adv. Mater.*, 1998, **10**, 1091; (*b*) A. C. Dillon, K. M. Jones, T. A. Bekkedahi, C. H. Kiang, D. S. Bethune and M. J. Heben, *Nature* (*London*), 1997, **386**, 377; (*c*) V. Krstic, J. Muster, G. S. Duesberg, G. Philipp, M. Burghard and S. Roth, *Synth. Met.*, 2000, **110**, 245; (*d*) M. Muris, N. Dafau, M. Bienfait, N. Dupont-Pavlovsky, Y. Grillet and J. P. Palmari, *Langmuir*, 2000, **16**, 7019, and references cited therein.

10 For example, see: (*a*) J. S. Mattson, H. B. Mark, M. D. Malbin, W. J. Weber and J. C. Crittenden, *J. Colloid Interface Sci.*, 1969, **31**, 116; (*b*) I. Moriguchi, S. Fushimi and N. Kaneniwa, *Chem. Pharm. Bull.*, 1970, **18**, 449; (*c*) H. Tamone, M. Atsushi and M. Okazaki, *J. Colloid Interface Sci.*, 1996, **177**, 384.

11 No change in the UV-vis spectra over 7 days was seen for aqueous 1% SDS solutions of: 1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 3-nitrotoluene, 3,4-dinitrotoluene, 2,4-dinitrotoluene, 1-bromo-4-nitrobenzene, 4-nitroacetophenone, 4-nitrobenzaldehyde, methyl 4-nitrobenzoate, 4-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 4-nitrocinnamic acid, 2-cyclohexen-1-one, 3-nitrobenzophenone, 1-nitronaphthalene, 2-nitronaphthalene, 1-naphthol, 2-nitro-1-naphthol, 1-naphthylacetic acid, phthalide, 2-nitrofluorene.

12 Aldrich Chem. Co. 'buckytubes', powdered as-produced cylinders.

13 S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature* (*London*), 1994, **372**, 159.

14 Beer–Lambert law: $A = \varepsilon cl$. For nitrobenzene ($\lambda_{max} = 267$ nm) at $t = 0$: $A = 2.3729$, $c = 1.62 \times 10^{-4}$ M, $\varepsilon = 14\,648$ M^{-1} cm^{-1}. At $t = 7$ days, $A = 1.9239$, $c = 1.31 \times 10^{-4}$ M. Thus, 1.55×10^{-7} mol or 0.02 mg was adsorbed from a 5 ml solution. For 4-nitrotoluene ($\lambda_{max} = 283$ nm) at $t = 0$: $A = 1.2865$, $c = 1.46 \times 10^{-4}$ M, $\varepsilon = 8812$ M^{-1} cm^{-1}. At $t = 7$ days, $A = 1.0643$, $c = 1.21 \times 10^{-4}$ M. Thus, 1.25×10^{-7} mol or 0.02 mg was adsorbed from a 5 ml solution.

15 R. J. Williams, J. N. Phillips and K. J. Mysels, *Trans. Faraday Soc.*, 1955, **51**, 728.

16 E. J. Wanless and W. A. Ducker, *J. Phys. Chem.*, 1996, **100**, 3207.

17 N. Pirinccioglu, F. Zaman and A. Williams, *J. Org. Chem.*, 2000, **65**, 2537.