

Formation and Characterization of Ethyl 2-Oxocyclo-pentanecarboxylate/Graphitic Oxide Intercalation Compounds

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Abstract. A study by X-ray diffraction, gravimetric adsorption, gravimetric and differential thermal analysis and Fourier transform infrared spectroscopy was made of the intercalation compounds which ethyl 2-oxocyclopentanecarboxylate (CBCP) forms with graphitic oxide. The interlamellar disposition of the organic molecule as well as the CBCP/graphitic oxide interaction is also discussed.

Key words: Graphitic oxide, ethyl 2-oxocyclopentanecarboxylate, gravimetric adsorption, FT-IR spectroscopy, intercalation compound.

1. Introduction

When certain ions or molecules become reversibly inserted in an acceptor matrix, generally a solid having a layered structure, intercalation compounds are obtained. A certain energy is required for an intercalation reaction to occur since the layers of the acceptor matrix must separate to allow the guest species to become installed. This consumption of energy is compensated by a contribution of energy resulting from the type of binding, which may be by electron transfer between the acceptor matrix and the intercalated species, a van der Waals type interaction or even an interaction due to the formation of hydrogen bonds such as in most cases of graphitic oxide.

Accordingly, intercalation processes are governed by both geometric and energetic requirements, the reaction being prevented when either of them is unfavourable [1].

Graphitic oxide (GO) is a compound of great scientific and technical interest since it has a layer structure and a strong capacity to adsorb polar molecules by interaction with the functional groups of its interlayer spaces [2–4]. Among other applications of GO it has been used as a semipermeable membrane for measuring osmotic pressure [5] or as a cathodic material in lithium batteries [6,7], which have the advantage of possessing a theoretical mass energy four or five times higher than the classic lead accumulators. It is also used in the manufacture of lubricants [8,9],

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for preparing fire-resistant foams [10] and in different catalytic reactions [11].

In the present work, the adsorption of a β -ketoester on GO was studied to investigate whether interlayer compounds are formed with such large molecules, as steric hindrance with the epoxy groups of the carbonaceous layer of GO would be expected in such circumstances. This was also investigated in order to check which group (keto or ester) is involved in the coordination of the adsorbate with the adsorbent. Taking into account the amount of polar liquid retained in the interlayer space as well as the surface area of the CBCP molecule, the values of the interlayer surface of GO accessible to the adsorbate were calculated and were found to be in good agreement with previous results [12–14] using several organophosphorus molecules.

2. Experimental Methods and Materials

The GO used in this work was obtained by oxidation of graphite (from Madagascar, 92–93% carbon content) in a sulphonitric mixture with KClO_3 according to the method of Staudenmaier [15]. The specific surface area, measured by the B.E.T. method is $36 \text{ m}^2\text{g}^{-1}$. The compound employed as adsorbent, ethyl 2-oxocyclopentanecarboxylate, $\text{C}_8\text{H}_{12}\text{O}_3$, (CBCP), supplied by Fluka with a 'technical' degree of purity, has the following properties [16]: boiling point 218°C at 704 mm Hg and 110°C at 16 mm Hg; density, 1.0781 g cm^{-3} ; refractive index 1.4519 at 20°C . The compound is soluble in ether and benzene and also in other organic solvents and is practically immiscible with water although it can be dissolved in solutions of potassium hydroxide.

The following procedures were used to form the intercalation compounds between GO and CBCP.

1. Impregnation at room temperature. Samples of GO were kept under impregnation conditions with CBCP for several days. X-ray powder photographs were recorded periodically to check for variations in the (d_{001}) basal spacing.

2. Impregnation and later desorption at room temperature. For this method a conventional gravimetric vacuum apparatus was used, equipped with an adsorption chamber containing a Jolly balance [17] which permitted the determination of the amount of CBCP retained in the interlayer space of the graphite oxide. The sample of graphite oxide, placed on an aluminium disc hung from the calibrated quartz spiral (38.5 cm g^{-1}), was outgassed at room temperature for 4 h until a constant degree of elongation was obtained. Afterwards, the CBCP was added to the sample of graphitic oxide and was maintained under impregnation at room temperature for 3 and 21 days in order to test whether the impregnation time might affect the stability of the possible interlayer compounds. After this time had elapsed the adsorption chamber was connected (at room temperature) to the vacuum system (about 10^{-4} Pa) to eliminate the excess of adsorbate not retained by the adsorbent. A decrease in the elongation of the spiral was observed over a period of time as a consequence of weight loss due to the evaporation of CBCP, until a constant

TABLE I

Interlayer spacing of GO after room temperature impregnation in CBCP for different times (days).

	0	3	9	28	37
d_1 (Å)	6.91	7.13	7.11	7.38	7.42
I_1 (%)	100	100	100	85.6	82.5
d_2 (Å)	–	9.48	9.56	8.61	9.07
I_2 (%)	–	31.8	36.5	100	100

position was reached.

3. Adsorption in an atmosphere of CBCP. In this process, a small beaker with CBCP was placed in the bottom of the adsorption chamber and the system was then outgassed for 30 min to remove the air. An increase in the length of the spiral was observed, thus indicating that the CBCP had been adsorbed by the GO.

Using a KBr pressed disc, infrared spectra were recorded on a Perkin–Elmer FT-IR M-1700 2B instrument. X-ray diffraction patterns were recorded on a Siemens model Kristalloflex 810 instrument using $\text{CuK}\alpha$ ($\lambda = 1.54050\text{Å}$) radiation and a graphite monochromator. The traces obtained by differential thermal analysis were recorded on a Perkin-Elmer model 1700 apparatus using a dynamic atmosphere of argon. The ^1H NMR spectra were obtained on a Bruker WP200 SY instrument (200 MHz) using deuterated chloroform as the solvent.

3. Results and Discussion

The CBCP molecule is a β -ketoester that displays keto–enol tautomerism. In order to elucidate which form the molecule adopts when the intercalation compound is produced, its NMR spectrum was recorded (Figure 1). The integrated spectrum shows the equilibrium to be displaced 77% towards the ketonic form in solution.

Table I shows that as the impregnation time is increased (method 1) two X-ray diffraction maxima appear, the first of them (assigned to the basal spacing of the graphite oxide) decreases in intensity and at the same time is displaced slightly towards greater distances. The second increases in intensity and its spacing reaches an equilibrium value of 9.07Å when the impregnation time is 37 days. This indicates an increase in the interlayer distance upon CBCP adsorption due to displacement of the water molecules originally existing in the interlayer space of the GO, although the existence of a fairly weak diffraction maximum around 7Å indicates that not all these molecules have been removed.

Figure 2 shows that the desorption process (method 2) takes place with a loss of weight, due to the evaporation of CBCP, that tends asymptotically towards a limiting value of adsorbate retained per gram of adsorbent, reached after several hours of treatment. The residual amount of CBCP is 197 mg g^{-1} for the 3 day

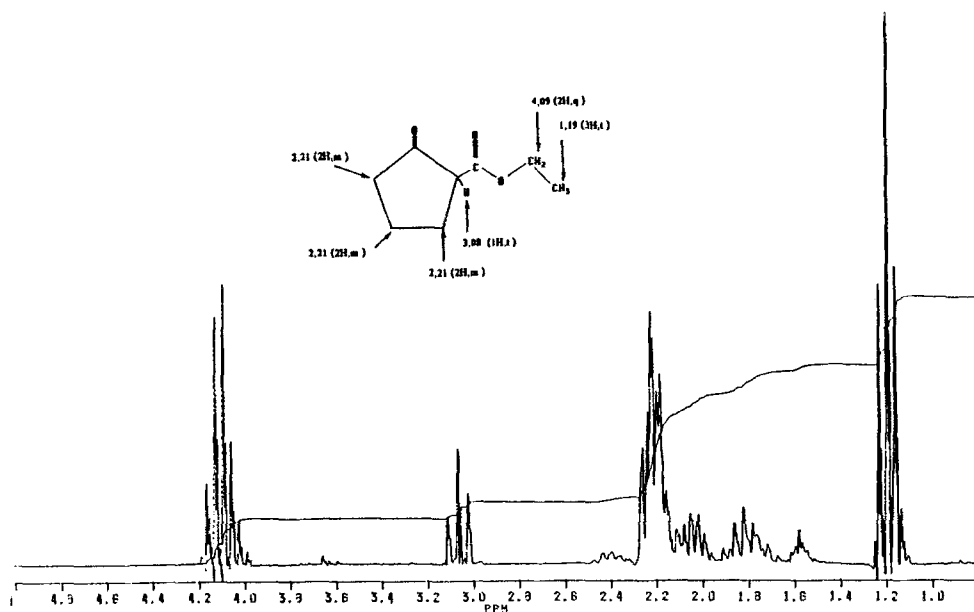


Fig. 1. ^1H NMR spectrum of CBCP in CDCl_3 .

impregnation and 407 mg g^{-1} for that of 21 days. The X-ray diffractograms of these samples and of GO are shown in Figure 3. The diffraction peak, observed at 9.5\AA , relative to samples subjected to a 3 day impregnation, increases in intensity when the impregnation time is 21 days. In this case, a single peak appears at 9.4\AA , corresponding to the basal spacing of the intercalation compound, this is analogous to the one that appeared after impregnation at room temperature (method 1). According to these results, it may be deduced that the impregnation of GO for 3 days results in intercalation of only some of the molecules of CBCP, without saturation of the whole surface accessible to the adsorbate; thus, molecules of intercalated CBCP (9.5\AA) coexist with molecules of water (7\AA). However, in the 21 day impregnation the accessible layer surface is completely occupied by molecules of CBCP, which is reflected in a clearly defined diffraction maximum at a greater basal spacing than that of the initial GO. These findings are consistent

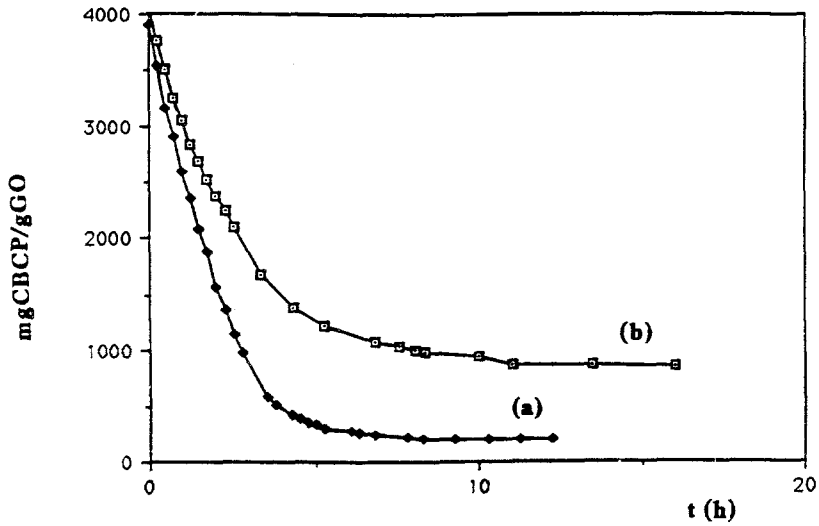


Fig. 2. Desorption isotherm (300 K) of GO impregnated for different times in CBCP: (a) impregnation for 3 days; (b) impregnation for 21 days.

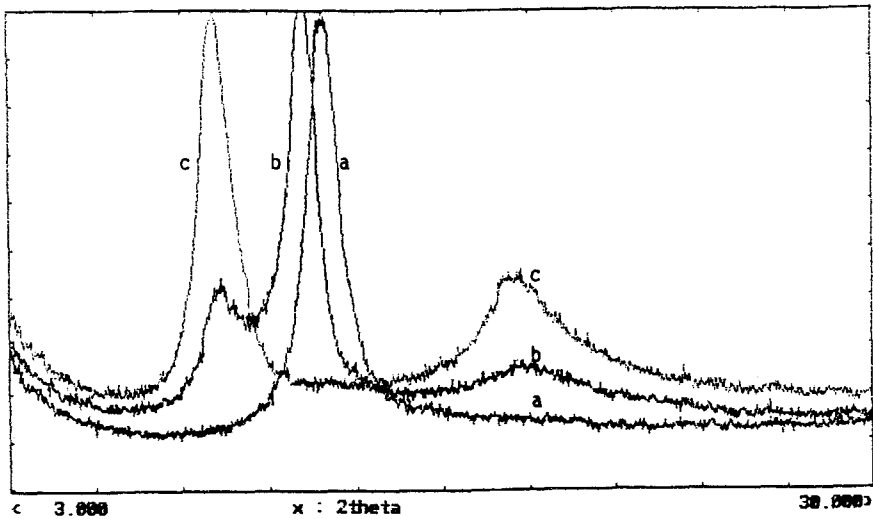


Fig. 3. X-ray diffractograms of GO (a) and of the intercalation compounds arising from GO impregnation in CBCP for 3 (b) and 21 (c) days, respectively, and later evacuation at room temperature.

with the amount of adsorbate retained. The small difference observed between the interlayer spacing when the intercalation compounds are obtained by impregnation at room temperature (9.05Å) and when obtained by impregnation followed by desorption at room temperature (9.4Å) can be attributed to a better ordering of the CBCP molecules in the interlayer spacing of the graphitic oxide, in the latter case

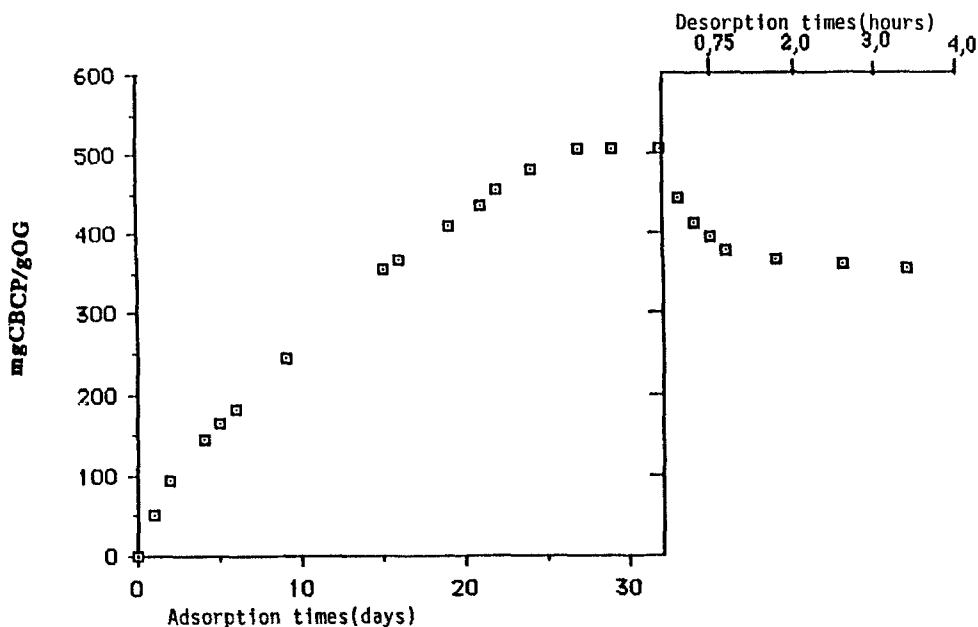


Fig. 4. Adsorption-desorption isotherms (300 K) from the gas phase of CBCP on GO.

due to the conditions of the dynamic vacuum and the lack of excess CBCP on the adsorbent.

Figure 4 represents the amount of CBCP adsorbed by GO as a function of time (method 3) when the adsorption is carried out in an atmosphere of CBCP. A progressive increase in weight can be noted which tends, in an asymptotic fashion, towards a limiting value that become practically constant after 28 days of treatment. In order to eliminate the CBCP that may remain deposited on the sample of graphitic oxide itself without having formed intercalation compounds, the CBCP container is withdrawn from the chamber and the system again outgassed. This led to a loss of weight which reached a stable value after 3 hours of treatment, corresponding to the amount of CBCP retained by graphite oxide of 356 mg g^{-1} . The X-ray diffraction analysis performed on these compounds, which were obtained in the presence of CBCP vapour, affords a basal spacing of 9.4 \AA , similar to that obtained by the other procedures.

To interpret these results it is necessary to know, apart from the structure of the adsorbent and the thickness of the beaded surface of GO, evaluated at 4.8 \AA [18], the molecular geometry of the adsorbate obtained with the use of models and molecular parameters [19,20]. From the results obtained, the most likely arrangement of the molecules of adsorbate to occupy the interlayer zone of GO would be a monolayer of CBCP molecules (Figure 5), arranged in such a way that the steric hindrance with the epoxide groups of the beaded layer would be minimum. This intercalation

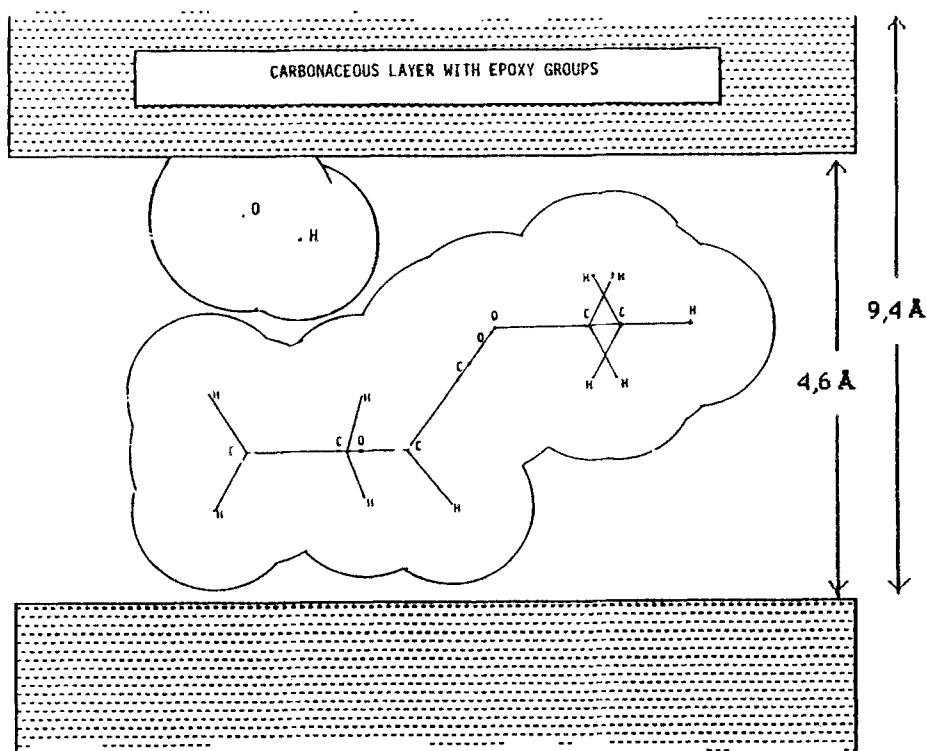


Fig. 5. Most probable orientation of the CBCP molecule in the interlayer space of GO.

compound is stable under the conditions produced in the process of adsorption and desorption (room temperature and 10^{-4} Pa).

The surface area of the CBCP molecule, obtained by planimetry, has a value of 48.0 \AA^2 . Likewise, using the formula developed by López-Conzález *et al.* [21] the values of the interlayer surface of the GO accessible to the adsorbate were calculated, giving a value of $1506 \text{ m}^2 \text{ g}^{-1}$ for the impregnation-desorption treatment at room temperature, and $1317 \text{ m}^2 \text{ g}^{-1}$ for the adsorption-desorption process. The first of these is consistent with the values reported in the literature [14,22]. However, the discordance of the second value may be due to the slow kinetics of the adsorption of CBCP molecules by graphitic oxide; hence, the time elapsed is insufficient for the whole of the accessible interlayer surface to be occupied by these molecules.

To determine the type of interaction between CBCP and GO in the intercalation compound, infrared spectroscopy was employed, in the $4000\text{--}400 \text{ cm}^{-1}$ range. The regions of the spectrum between $1800\text{--}800 \text{ cm}^{-1}$ and $3500\text{--}2500 \text{ cm}^{-1}$ are those that reveal the greatest differences between the free and associated compounds.

Figure 6 shows the IR spectra of GO, CBCP and the CBCP/GO intercalation compound in the $1800\text{--}800 \text{ cm}^{-1}$ region. In the intercalation compound it

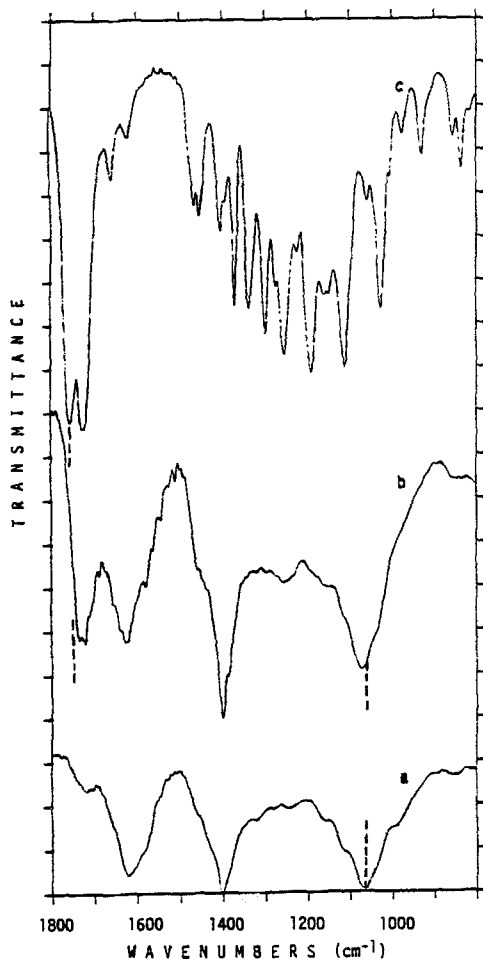


Fig. 6. FT-IR spectra (1800–800 cm^{-1} region) of GO (a), the CBCP/GO intercalation compound (b) and CBCP (c).

is possible to observe bands characteristic of pure graphitic oxide and CBCP adsorbed as such (23–27) [1626 cm^{-1} , ($\nu_{\text{C}=\text{C}}$); 1401 cm^{-1} , ($\delta_{\text{C}-\text{O}-\text{H}}$); 1253 cm^{-1} , ($\nu_{\text{C}-\text{C}-\text{C}}$); 1386 cm^{-1} , (δ_{simCH_3}); 1258 cm^{-1} ($\nu_{\text{C}-\text{C}-\text{C}}$)]. The most important differences observed are: an increase in the intensity of the band at 1719 cm^{-1} with respect to free graphitic oxide, owing to the presence of the C=O groups of the CBCP; also, the band that appeared in the free CBCP at 1757 cm^{-1} is seen to be shifted to 1736 cm^{-1} and overlaps the previous one, suggesting a decrease in the electron density of the C=O bond of the ester and indicating that the coordination of the adsorbate with the adsorbent is produced by this group. On the other hand, in the stretching vibration region of the C–O bond, a sharp and intense peak is

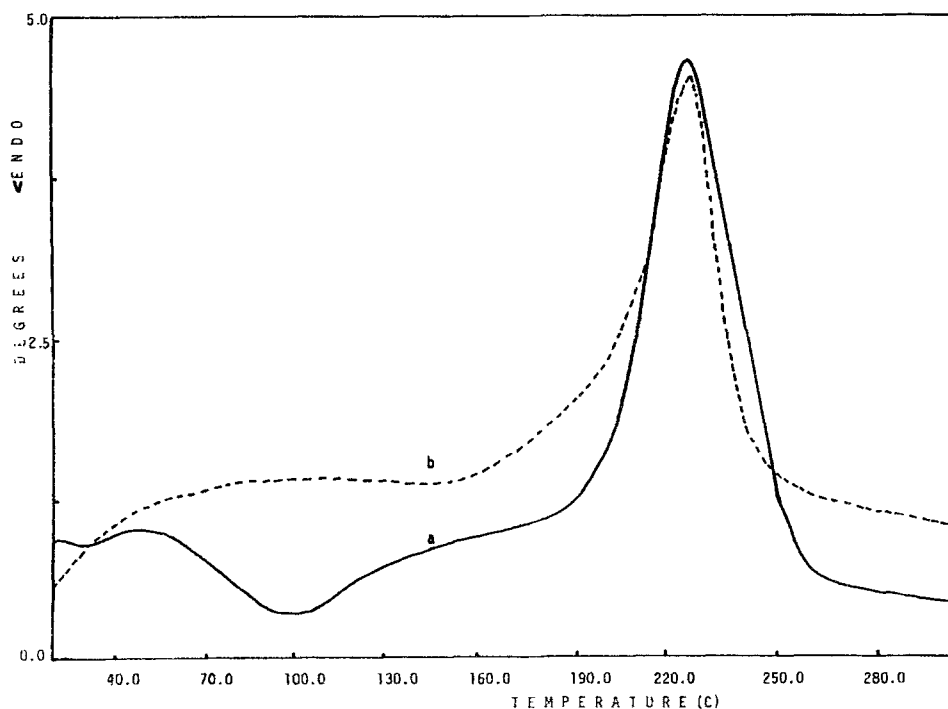


Fig. 7. Differential thermal analysis of GO (a) and the CBCP/GO intercalation compound (b).

seen at 1093 cm^{-1} ; that is, at a significantly higher frequency than that of free graphitic oxide (1069 cm^{-1}). This points to the CBCP/GO interaction taking place through hydrogen bonds between the hydroxyl groups of the GO and the carbonyl group of the CBCP ester. This interaction confirms the variation in frequency, mentioned above, that takes place in the stretching vibration of the free carbonyl group (1757 cm^{-1}) and intercalate (1736 cm^{-1}) of the CBCP, respectively.

The FT-IR spectrum of the intercalation compound displays, in the $3500\text{--}2500\text{ cm}^{-1}$ region, bands characteristic of the adsorbed compounds as such: (3397 , 3250 cm^{-1} , $\nu_{\text{O-H}}$, due to uncoordinated and coordinated by hydrogen bonds, respectively; 2925 cm^{-1} , $\nu_{\text{C-H}}$, of the CBCP). Additionally, a slight narrowing of the band corresponding to the stretching vibration of the OH groups is observed due to a smaller contribution of the hydrogen bonds in the intercalation compounds with respect to GO, where the interlayer water molecules are coordinated with the layers by hydrogen bonds [28].

The thermal stability of the compounds obtained was determined by differential thermal analysis (DTA). Figure 7 compares the recordings obtained from the DTA of graphitic oxide and the intercalation compound obtained; it is possible to observe an exothermic peak at 226°C owing to the decomposition of the graphitic oxide [25]. However, the endothermic peak appearing in the graphitic oxide at 90°C due

to dehydration, is not present in the intercalation compound, indicating the absence of water molecules in this compound because they are displaced out of the interlayer space by the CBCP molecules.

4. Conclusion

In the present work the formation of the intercalation compounds CBCP/GO was investigated. Analysis by X-ray diffraction of samples subjected to the three types of treatment (impregnation at room temperature, impregnation and later desorption at room temperature and adsorption in an atmosphere of adsorbate vapour) yield a basal spacing around 9.4Å, which can be attributed to the formation of an intercalation compound (monolayer) formed by CBCP molecules in the interlayer of the GO.

The infrared spectra recorded for these compounds show as the most significant data the shifts of the C=O stretching mode of the CBCP ester group, from 1757 cm⁻¹ (observed in the free molecule) to 1736 cm⁻¹ in the intercalation compound, and that of the C–O stretching mode in the graphitic oxide, from 1068 cm⁻¹ (observed in free GO) to 1093 cm⁻¹ in the intercalation compound. These shifts clearly show that the interaction of CBCP with the adsorbent takes place through hydrogen bonds between the abovementioned groups (C=O···H–O–C).

From the amount of adsorbate retained by GO (around 400 mg g⁻¹) as well as the surface covered by a molecule of CBCP (48.0Å²), the accessible surface area of GO to CBCP is found to be close to 1500 m² g⁻¹ in good agreement with that reported in the literature for well oxidized graphitic oxide.

References

1. M. Stanley Whittingham and A.J. Jacobson: *Intercalation Chemistry*, Academic Press, London (1982).
2. D. Hadzi and K. Novak: *Trans. Faraday Soc.* **51**, 1614 (1955).
3. F. Aragon de la Cruz and J.M. Cowley: *Acta Crystallogr.* **16**, 531 (1953).
4. M.A. Bañares, M.E. Pérez, V.S. Escribano, and R.J. Ruano: *Carbon* **22**, 465 (1984).
5. U. Hofman and A. Weiss: *Brevet Allemand D.R.P.* 847363 (1952).
6. P. Touzain, R. Yazami and J. Maire: *J. Powder Sources* **14** (1–3), 99–104 (1985).
7. J. Rouxel and R. Brec: *Annual Rev. Material Sci.* **16**, 137 (1986).
8. H. Kuhlmann: *Brevet Français*, 964784 Aofit (1960).
9. Doi Tei and Shiba Satoshi: *Jpn. Kokai Tokkyo Koho JP* 63, 23, 993 [8823, 993] (Cl. C10M111/04), (01 Feb 1988), Appl. 86/165,630 (16 Jul 1986).
10. Kuga Shigeo and Katsuki Koretoshi: *Jpn. Kokai Tokkyo Koho JP* 01, 311, 137 [89 311, 137] (Cl. 0859/04), (15 Dec 1989), Appl. 88/141, 029 (08 Jun 1988).
11. J.F. Tempere and B. Imenik: *Bull. Soc. Chim. Fr.* 4227 (1970).
12. M.A. Bañares, L.V. Flores, M.E. Pérez, R.J. Ruano, and V.S. Escribano: *Agrochimica* **29**, 418 (1985).
13. M.A. Bañares, L.V. Flores, M.E. Pérez, R.J. Ruano, and V.S. Escribano: *Agrochimica* **29**, 435 (1985).
14. V. Sánchez Escribano, M.A. Bañares Muñoz, and J.M. Sánchez Conejero: *Chemosphere* **22**, 905 (1991).
15. L. Staudenmaier: *Ber.* **31**, 1481 (1898).

16. *Handbook of Chemistry and Physics*, CRS Press. 63rd. Edition (1982–83).
17. J.W. Mac Bain and A.M. Bakr: *J. Am. Chem. Soc.* **48**, 690 (1926).
18. D.M.C. Mc Ewan and J. Cano Ruiz: *An. Quim.* **54B**, 43 (1958).
19. D.D. Swank, G.F. Needham, and J.R.D. Willet: *Inorg. Chem.* **18**, 761 (1979).
20. N.N. Greenwood and A. Earnshaw: *Chemistry of the Elements*, Pergamon Press, N.Y. (1984).
21. J.D. López González, A. Martín Rodríguez, and F. Domínguez Vega: *Carbon* **9**, 279 (1971).
22. J.D. López González, M.A. Bañares Muñoz, and A. Ramírez Saenz: *Quim. Ind.* **16**, 3 (1970).
23. E. Pretsch, T. Clerc, J. Seibl, and W. Simon: *Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos*, Ed. Alhambra (1980).
24. T. Conley: *Espectroscopía infrarroja*, Ed. Alhambra (1979).
25. A. Pacault: *Les Carbones*, Ed. Masson et Cie. Paris (1965).
26. V. Sánchez Escribano, G. Busca, and V. Lorenzelli: *J. Phys. Chem.* **94**, 8939 (1990).
27. V. Sánchez Escribano, G. Busca, and V. Lorenzelli: *J. Phys. Chem.* **95**, 5541 (1991).
28. L.J. Bellamy: *The Infrared Spectra of Complex Molecules*, Ed. Chapman & Hall, 3rd Edition (1978).