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Thermal stability of solid dispersions of naphthalene derivatives with β-cyclodextrin and β-cyclodextrin polymers

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Abstract

The thermal stabilities of some naphthalene derivatives (1-naphthyl acetate, 2-acetylnaphthalene, 1-naphthol) in β-cyclodextrin (β-CD) inclusion complexes and in β-CD-containing polymeric systems (Polyβ-CD) have been studied using thermal and thermogravimetric analyses and infrared spectroscopy. In β-CD systems, the stability of the 1-naphthyl acetate complex is lower than that of the 2-acetylnaphthalene complex, and both are more stable than the corresponding physical mixtures. For Polyβ-CD systems, the solid dispersions result much more stable than the corresponding β-CD ones, both at room temperature and at 60 °C. In the case of Polyβ-CD, besides the inclusion within CD cavities, the interaction of the guest with the crosslinking network confers an additional stability against volatilization. In contrast, an analogous crosslinked polymer prepared using sucrose instead of β-CD does not retain noticeable amounts of the naphthalene derivatives.

Keywords: Cyclodextrins; Cyclodextrin polymers; Naphthalenes

1. Introduction

Beta-cyclodextrin (β-CD) is a torus-shaped natural cyclic oligosaccharide, having seven glucopyranose units linked by α-1,4-glycosidic bonds, with two hydrophilic rims and a cavity less polar than water. Its unusual structure gives the β-CD the ability to form inclusion complexes, both in solution and in solid phase, through non-covalent interactions with molecules that fit into the cavity. The stability of such complexes is mainly attributed to van der Waals and hydrophobic interactions [1], although the substitution of a polar group in the guest compound can influence the stability of the complex, by establishing either dipolar or hydrogen bonding interactions [1–3]. These inclusion complexes may confer desirable properties on the guest molecules such as an increased stability against hydrolysis or high temperatures, an enhanced aqueous solubility, and the masking of unpleasant tastes or odors of various chemicals. This encapsulating ability has found countless applications in fields such as drug delivery, water purification, food industry, analytical methods, etc. [4].

β-CD can be crosslinked with polyfunctional reagents such as aldehydes, ketones, isocyanates or epoxides, to obtain water insoluble polymers that capture molecules from aqueous solutions. One of the most used crosslinking agents is epichlorohydrin. The polymers synthesized by condensation between β-CD and epichlorohydrin have been employed in many applications [5]. Because of their properties these polymers are used in separation columns for chromatography, in pharmaceutical and food industries, for synthetic purposes (in catalysis), for wastewater treatment, etc. [6,7]. In this case, the sorption mechanism involves several kinds of interactions as proposed by several authors [7,8]. Besides the inclusion within β-CD cavities, a physicochemical adsorption in the polymer network can also take place.

Thermal analysis has been used as a tool in the characterization of CDs and their inclusion complexes [9]. Among the different CDs, β-CD is the most widely used because it provides a better fit to a great variety of aromatic hydrocarbons and their derivatives. Its thermoanalytical profile can be structured in four stages: (1) water loss from ambient temperature up to 120 °C (depending on the experimental arrangements: kind of crucible and lid, atmosphere. . .); (2) a plateau region; (3) thermal degradation, that starts above 250 °C in solid phase and continues for the liquid after fusion; (4) ignition, that takes place in air

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above 300 °C. The thermogravimetric curve is flat between 120 and 280 °C (i.e. there is no mass loss), but the calorimetric curve shows small endo and/or exothermic peaks at 210–240 °C. The plateau region is especially interesting in the study of cyclodextrin dispersions if changes in the patterns corresponding to the guests can be detected. The thermal degradation of cyclodextrins [10] and the stability of their complexes [11] have been already studied. Nevertheless, to our knowledge, the thermal stability of cyclodextrin polymers and their dispersions with guest molecules have not been investigated. In this study, we analyse some naphthalene derivatives dispersed in β-CD and in β-CD-containing polymeric systems (Polyβ-CD) in order to contrast their behaviors, i.e. we intend to find out whether the polymeric network has an influence on the stabilization of these volatile compounds.

2. Experimental section

2.1. Materials

Three naphthalene derivatives (Scheme 1) were studied: 1-naphthyl acetate (99+%) from Acros Organics, 2-acetylnaphthalene (99%) from Aldrich and 1-naphthol (99+%) from Merck. β-CD was kindly donated by Roquette (Laisa España S.A.), sucrose was from Merck and epichlorohydrin from Aldrich. NaOH and 1-propanol were from Panreac Química S.A., Spain. All of the reagents were used as received.

2.1.1. Preparation of polymers

Two insoluble polymeric resins were prepared by reticulation of either β-CD or sucrose (for the sake of comparison) using epichlorohydrin as a crosslinking agent in a NaOH/water medium [12].

In order to obtain the β-CD polymer, β-cyclodextrin (58 g) was mixed with the same amount of water in a thermostated reactor vessel. Twelve milligrams of $NaBH_4$ were added to avoid the oxidation of β-CD. Epichlorohydrin (40 mL, 47.32 g) was carefully added at 50 °C with stirring (200 rpm) during four minutes. When β-CD and epichlorohydrin were mixed, 65 mL of 40% aqueous NaOH solution (w/w) were added dropwise, keeping the temperature at 50 °C. The stirring was continued during the addition of NaOH for 1 h at constant temperature, until the gel point was reached. Then, 1 L of water was added to the reactor vessel in order to stop the reaction, deactivating the crosslinker excess. The stirring continued for one hour while cooling the product down to room temperature. After neutralizing the alkaline medium with a dilute HCl aqueous solution, the resin was washed several times with water and ethanol. Finally, after drying the resin at 60 °C for 3 days, 61.5 g of the crosslinked β-cyclodextrin polymer (Polyβ-CD) were obtained (yield 69%).

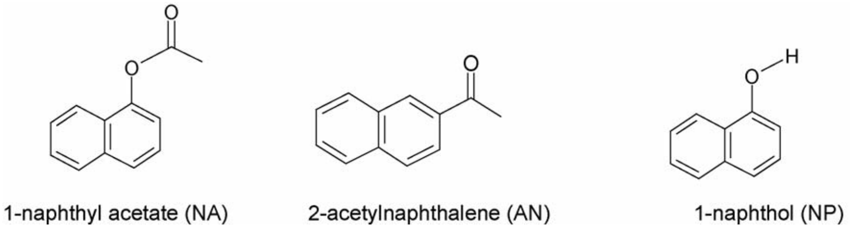
The sucrose insoluble polymer was prepared using 10 g of sucrose and 2 mg of $NaBH_4$, mixed with 10 mL of water and dissolved in 12 mL of an aqueous NaOH solution (40% w/w) in a conical flask. The temperature was kept close to 25 °C using a thermostated bath and 29.7 g of epichlorohydrin were added. The dispersion was mixed with a magnetic stirrer. After neutralized, washed, and dried as in the case of Polyβ-CD, 8.85 g of the crosslinked sucrose polymer (PolySuc) were obtained (yield 27%).

The polymers were characterized by infrared spectroscopy, thermal analysis, elemental analysis, water uptake, and phenol and naphthol sorption. The characterization results for both polymers are shown in Table 1. Elemental analysis of carbon and hydrogen was recorded on a LECO CHN-2000 analyzer (using samples of ca. 0.180 g) to elucidate the amount of β-CD or sucrose in the polymer. We have used the water content of each polymer measured by thermogravimetric analysis as a parameter for the calculation, so the results in Table 1 correspond to the anhydrous polymers.

For the sorption characterization of the polymers, 0.150 g of the resin were mixed with 50 mL of an aqueous solution of phenol or 1-naphthol (5.32×10^{-4} M) on a capped bottle, at 25 °C under agitation in a water bath. UV measurements of the supernatant were performed in a Hewlett Packard 8452A spectrophotometer, and the sorption capacities were calculated.

2.1.2. Preparation of solid dispersions

The samples were prepared by solvent evaporation following a method described previously [13]. The naphthalene derivatives were mixed with either β-CD or the polymers in 15 mL of 1-propanol/water solutions (1/2, v/v). After 3 h, the agitation was stopped and the solvents evaporated in a vacuum desiccator at 24 °C to obtain the solid dispersions, using a saturated atmosphere of the corresponding pure naphthalene derivative (to accomplish this task, a small amount of the pure derivative is placed inside the desiccator). A 1:1 molar ratio of the naphthalene derivative and β-CD or sucrose was used at 24 °C, taking into account the contents of β-CD or sucrose in the case of the polymers. Besides, for 1-naphtyl acetate and 2-acetylnaphthalene, 2:1 and 1:2 molar ratios were also prepared. For the Polyβ-CD and PolySuc systems, a second preparative method was also used: polymer particles embedded in aqueous dispersions of the naphthalene derivative were filtrated and dried, after saturation with the sorbate. In this method, 0.100 g



Scheme 1. Atom-and-bond representations of naphthalene derivatives.

Table 1
Characterization results for epichlorohydrin/β-CD and epichlorohydrin/sucrose polymers (Polyβ-CD and PolySuc, respectively)

Polymer	C (%)	H (%)	Crosslinker amt. (g/g of polymer)	Water loss at 125 °C (%)	Apparent swelling (mL/g of polymer)	Water uptake (g/g of polymer)	Naphthol sorption (μmol/g)	Phenol sorption (μmol/g)
Polyβ-CD	44.2	7.0	0.298	7.3	6.9	3.6 ± 0.2	157.87	47.05
PolySuc	43.9	6.9	0.290	4.8	6.9	2.8 ± 0.2	29.06	14.15

of polymer were stirred for 3 h in a flask containing 40 mL of an aqueous naphthalene derivative solution (ca. 5.3×10^{-4} M). For 1-naphthyl acetate we also used a variant of this method using 1-propanol/water as the solvent (1/2, v/v), in order to increase the solute concentration. Physical mixtures of naphthalenes and β-CD or Polyβ-CD were also prepared in the same molar ratios.

2.2. Measurements

The polymers and their dispersions with the sorbates were evaluated by simultaneous differential thermal and thermogravimetric analysis and also by infrared (FTIR) spectroscopy. The samples were measured as prepared and their evolutions at room temperature and at 60 °C were followed by analyzing aliquotes of the stored samples.

Differential thermal (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) curves were collected using a TGA-sDTA 851 Mettler Toledo thermoanalyzer with pierced aluminum crucibles, at 5 K/min heating rate under static air atmosphere, from ambient temperature to 450 °C for the polymeric solid dispersions, and up to 400 °C for the β-CD ones. The sample weights ranged between 10 and 15 mg.

The infrared spectra were recorded using a Nicolet-FTIR Avatar 360, with OMNIC E.S.P. software [14]. The resolution was 2 cm^{-1} and the spectra were the result of averaging 100 scans. All the measurements were carried out at 20 ± 1 °C. The KBr disk method has been used for the solid samples. The pellets were prepared by mixing the samples with KBr with a pestle on an agate mortar (1–2 mg and 100–150 mg, respectively), dried under a lamp, and compacted with a hydraulic press. Multiple curve fitting using Origin 5.0 [15] was performed for the carbonyl stretching bands of the spectra following the procedure described in a previous paper [13].

3. Results and discussion

For a better analysis of the results, three stages for the thermal patterns are considered [10]: (a) below 150 °C, loss of

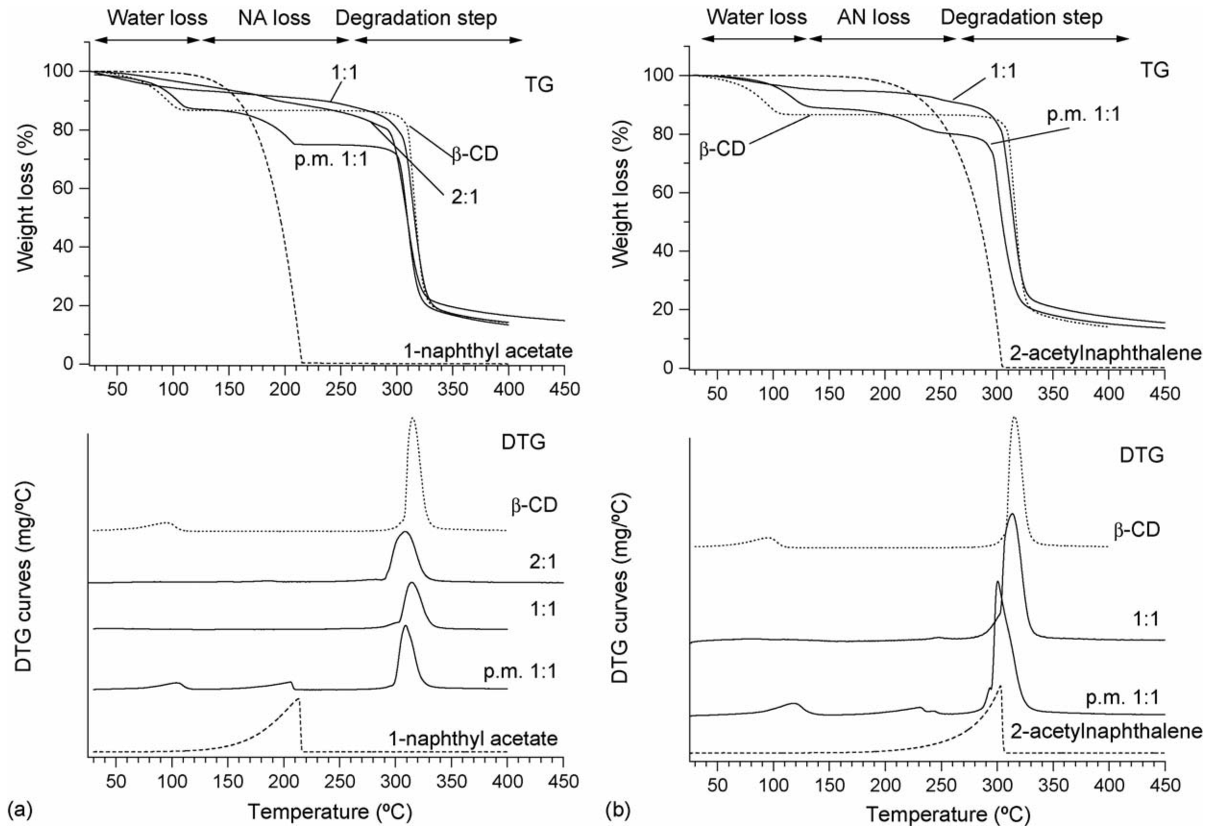


Fig. 1. TG and DTG curves of pure β-CD and (a) 1-naphthyl acetate:β-CD dispersions; (b) 2-acetylnaphthalene:β-CD dispersions (pure NA and AN and their physical mixtures, p.m., are shown for comparison).

solvent (water and/or propanol), and melting of the naphthalene derivative (detected also as an endotherm in DTA patterns); (b) 150–285 °C, loss of the naphthalene derivative by volatilization in the TG pattern (endotherm in DTA); (c) above 285 °C, degradation of β-CD or Polyβ-CD.

We have used FTIR spectroscopy to study the stability of the mixtures at room temperature and at 60 °C for the carbonyl derivatives. The presence of the carbonyl band can be utilized as the reference to easily follow the evolution of the solid dispersions. The stability is more critical for 1-naphthyl acetate systems, so we have focused our attention on these mixtures.

3.1. β-CD systems

The results of both thermal and thermogravimetric analyses of the dispersions of β-CD with 1-naphthyl acetate and 2-acetylnaphthalene are presented in Figs. 1 and 2. As can be seen in the thermogravimetric patterns of Fig. 1, the complexes lose less water than pure β-CD. This effect could be attributed to naphthalene molecules replacing water molecules in the cyclodextrin cavity. Besides, neither the fusion peaks (Fig. 2) nor the mass loss steps (Fig. 1) corresponding to the naphthalene derivatives are clearly detected. There seems to be a gradual mass loss over 180 °C, that should be caused by a slow evaporation of the sorbate. In contrast, the changes in the patterns are evident for the physical mixtures of the naphthalene derivatives and β-CD. The complete disappearance of the melting endotherm of the guest in DTA curves supports the idea that an inclusion complex has been obtained [16]. An interaction at the molecular level causes the amorphization of the aromatic derivative, although other techniques must be employed to prove the inclusional nature of the interaction. This endotherm (ca. 40 °C) does not disappear in the 2:1 dispersions (Fig. 2), evidencing an excess of the pure naphthalene derivative for the mixtures of this stoichiometry. Finally, the degradation pattern of β-CD in the NA complex (1:1 stoichiometry) is close to that of pure cyclodextrin, whereas for the AN system the differences are more evident (see Figs. 1(b) and 2(b)). The physical mixture of 2-acetylnaphthalene shows also some differences with the final stage of the pattern of pure β-CD. This is probably related to the fact that the volatilization occurs close to the degradation of β-CD.

As shown in our previous work [13], the stability against volatilization of the 1-naphthyl acetate complex with β-CD is lower than that of acetylnaphthalene (as occurs for the volatilization of the pure compounds), although both complexes are more stable than their corresponding physical mixtures. For 1-naphthyl acetate, FTIR spectra show that the relative intensity of the carbonyl band for the complex decreases at room temperature after several days. At 60 °C this process occurs faster: several hours suffice to evaporate part of the guest from the solid dispersion. This is not the case for AN:β-CD complexes. The spectra of dispersions kept at room temperature remained unchanged for months.

3.2. Polyβ-CD systems

Among the different methods tested for loading the polymer with the guest molecules, the best results were achieved by evaporation from 1-propanol/water solutions (see Section 2). The results are more favorable than those of the filtration method, i.e. a higher amount of the naphthalene derivative is retained. In the filtration method, the variant using aqueous solutions yields better results than the 1-propanol/water mixtures because of the affinity of the naphthalene derivatives for less polar solvents. Nevertheless, the higher solubility of the naphthalene derivatives in 1-propanol/water does not hinder the sorption by the polymer in the evaporation method. Moreover, using a 10:1 ratio of NA:Polyβ-CD in a propanol/water solution, the amount retained by the polymer after filtration is less than that obtained from the solvent evaporation of a 2:1 NA:Polyβ-CD mixture.

Fig. 3 shows the thermogravimetric results for the naphthalene derivatives (NA and AN) mixed with Polyβ-CD. In the thermal patterns, no significant differences can be detected in the solvent loss step. In contrast to what it was observed for β-CD systems, in this case most of the solvent sorbed in the pure polymers (water and/or propanol) can be retained by the polymeric networks, and just a small amount is replaced inside the

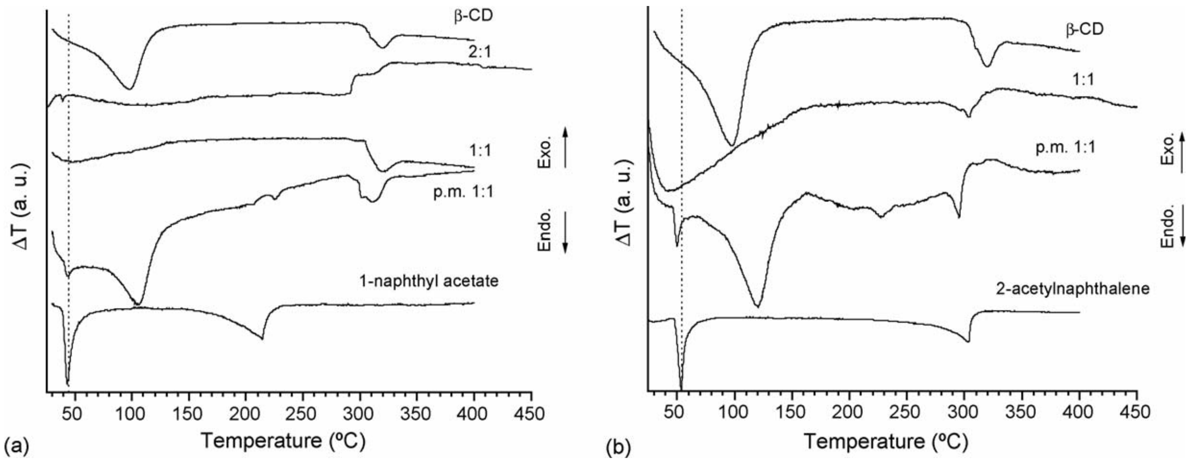


Fig. 2. DTA curves of pure β-CD and (a) 1-naphthyl acetate:β-CD dispersions; (b) 2-acetylnaphthalene:β-CD dispersions. (Broken lines: melting of pure NA and AN).

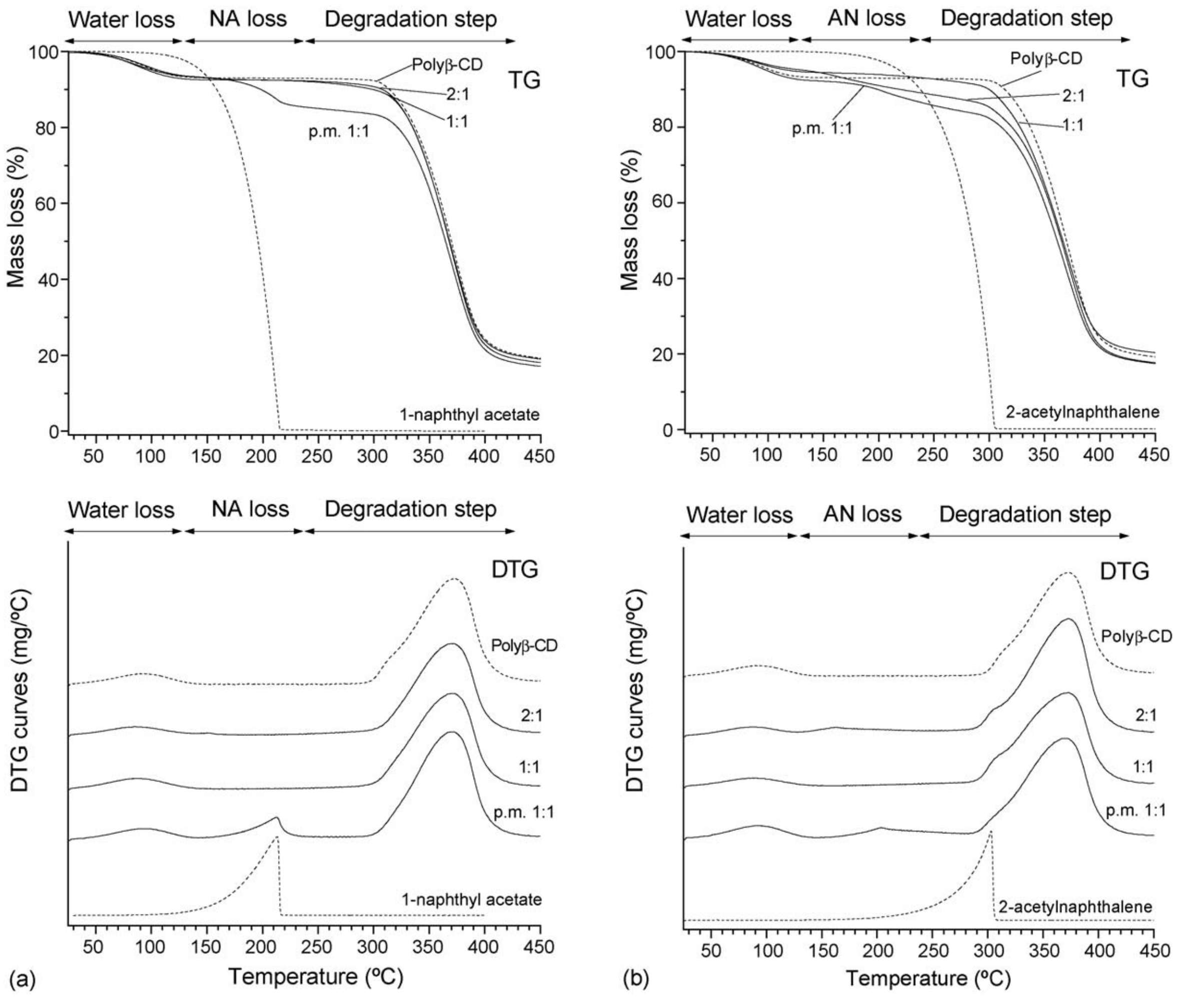


Fig. 3. TG and DTG curves of pure Polyβ-CD and (a) 1-naphthyl acetate:Polyβ-CD dispersions; (b) 2-acetylnaphthalene:Polyβ-CD dispersions (pure NA and AN and their physical mixtures, p.m., are shown for comparison).

CD cavities by the naphthalene guest molecules. On the other hand, the degradation pattern of Polyβ-CD is scarcely modified in the solid dispersions. For the 1-naphthol system (not shown) a contribution due to volatilization has also to be considered. The most important differences are found in both the naphthalene derivative melting peak and its mass loss step (NA: ca. 40 °C; AN: ca. 50 °C, NP: ca. 95 °C), that are absent in the 1:1 solid dispersions with Polyβ-CD, as occurred with β-CD. These results confirm that there is an intimate mixing between the guest molecules and the polymeric matrix (the naphthalene

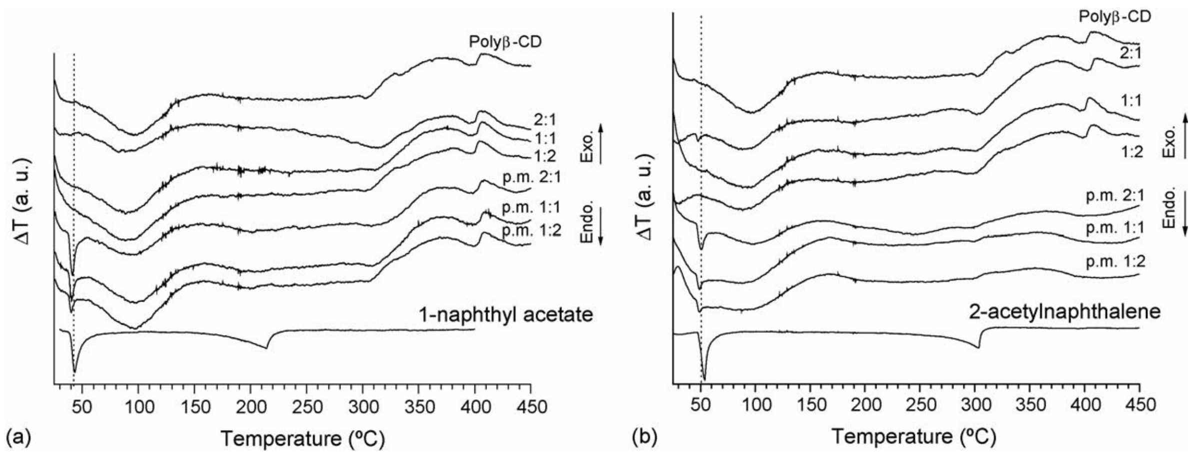


Fig. 4. DTA curves of pure Polyβ-CD and (a) 1-naphthyl acetate:Polyβ-CD dispersions; (b) 2-acetylnaphthalene:Polyβ-CD dispersions.

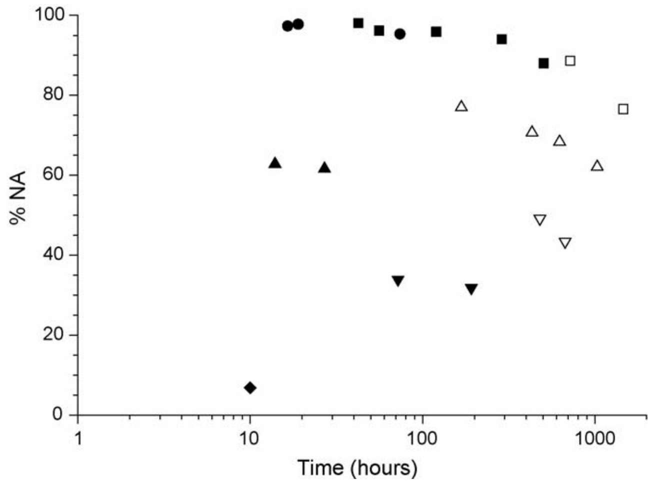


Fig. 5. Release of 1-naphthyl acetate from β-CD and Polyβ-CD dispersions at room temperature and at 60 °C. (△) β-CD 1:1 room temperature; (▲) β-CD 1:1 60 °C; (▽) β-CD 2:1 room temperature; (▼) β-CD 2:1 60 °C; (●) Polyβ-CD 1:1 60 °C; (□) Polyβ-CD 2:1 room temperature; (■) Polyβ-CD 2:1 60 °C; (♦) PolySuc 2:1 60 °C.

crystalline phase is not detected) and also the stabilization of the aromatic compound (its volatility is significantly diminished). It could be argued that the disappearing of the melting peaks could be due to the volatilization of the naphthalene derivatives. An experiment performed stopping the heating scan at 285 °C helps to discard this possibility. The subsequent infrared spectra show that the naphthalene derivatives remain in the dispersion even at these high temperatures, when the degradation of the polymer is about to start. DTA curves (Fig. 4) show that the 2:1 dispersions have different patterns for 1-naphthyl acetate and 2-acetylnaphthalene. The melting endothermic peak disappears for the former dispersion but not for the latter. This result supports the idea of an amorphous or microcrystalline nature for the uncomplexed NA guest. A slope in the DTA and TG curves also indicate some mass loss, probably that of the uncomplexed guest. In contrast, AN 2:1 dispersion shows a melting peak corresponding to a crystalline excess. NA does not totally penetrate the cyclodextrin cavity (it is placed in an equatorial position [17]) and the protruding part can form hydrogen bonds with the polymer network. In this way, the interaction NA:polymer is more favorable than that for AN.

For Polyβ-CD systems, the solid dispersions result much more stable, both at room temperature and at 60 °C, than those corresponding to β-CD systems. The stability of NA:Polyβ-CD samples is in the order of days at 60 °C and months at room temperature while for the β-CD system is of a few hours and several days, respectively. This is an important result, specially for 1-naphthyl acetate, because of its high volatility. The evolutions of the studied dispersions both at room temperature and at 60 °C are shown in Fig. 5. As can be seen, NA:Polyβ-CD dispersions result more stable than β-CD dispersions at both temperatures. In fact, the evolution for the NA:Polyβ-CD 1:1 dispersion at room temperature is not shown in the figure because the area of the carbonyl band is scarcely modified in 2 months. Even at 60 °C only a 5% was lost, while 1:1 NA:β-CD dispersion loses almost 40% in 13 h and becomes more stable after that (only an additional 1% is lost in 24 h). The same diminution is attained for this dispersion at room temperature in ca. 40 days. The evolution of 2:1 NA:β-CD is too fast in the beginning because there is an excess of pure NA that evaporates easily (66% lost in ca. 3 days), and then the evolution is slow as in the case of the 1:1 dispersion. In contrast, the 2:1 NA:Polyβ-CD dispersion does not lose the guest so easily: in 42 days it has lost 23% of the carbonyl area. This indicates that the “excess” of NA in this dispersion does not evolve like pure NA and that there has to be some kind of interaction with the polymeric network.

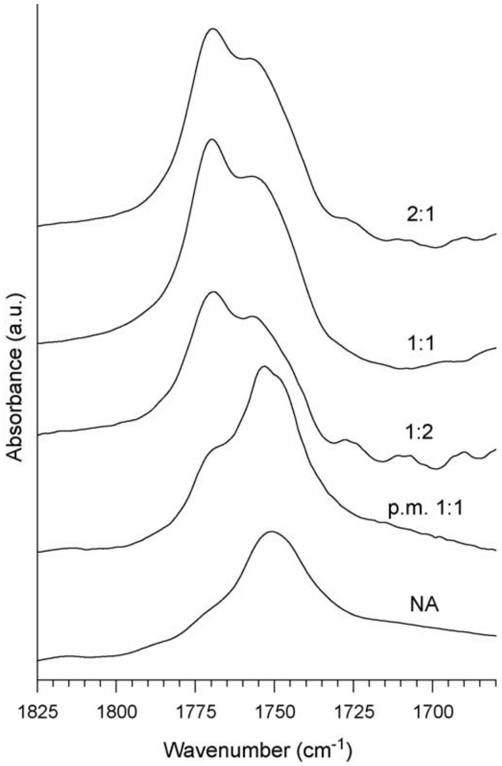


Fig. 6. FTIR spectra of 1-naphthyl acetate mixtures with Polyβ-CD in the carbonyl stretching region after subtraction of the Polyβ-CD or β-CD contribution, respectively, (pure 1-naphthyl acetate is shown for comparison). Spectra scaled using the 1-naphthyl acetate band at 1600 cm^{-1} as the reference.

As shown in Fig. 6, 1-naphthyl acetate FTIR spectra have two carbonyl contributions. This effect was attributed to a result of two different environments in our previous work [13]. The low wavenumber contribution is attributable to the associated carbonyls, via hydrogen bonds, with β-CD hydroxyl groups in the case of the cyclodextrin dispersions [2,18,19]. The ‘free’ carbonyls, i.e. those not attached to hydroxyl groups, are detected at higher wavenumbers. The guest molecules associated via hydrogen bonding seem to be attached to the cyclodextrin in a stronger fashion. The modifications of the carbonyl band shapes are not the same for β-CD and Polyβ-CD systems, i.e. the ratio of the contributions, “free” and “hydrogen-bonded” carbonyls, evolves in a different way. Thus, while for β-CD systems during the first stages the free carbonyls diminish and the associated contribution remains unchanged, for Polyβ-CD systems both contributions diminish together (not shown).

As can be seen in Fig. 6, the amount of “associated” carbonyl groups (lower wavenumber contribution) is high for Polyβ-CD

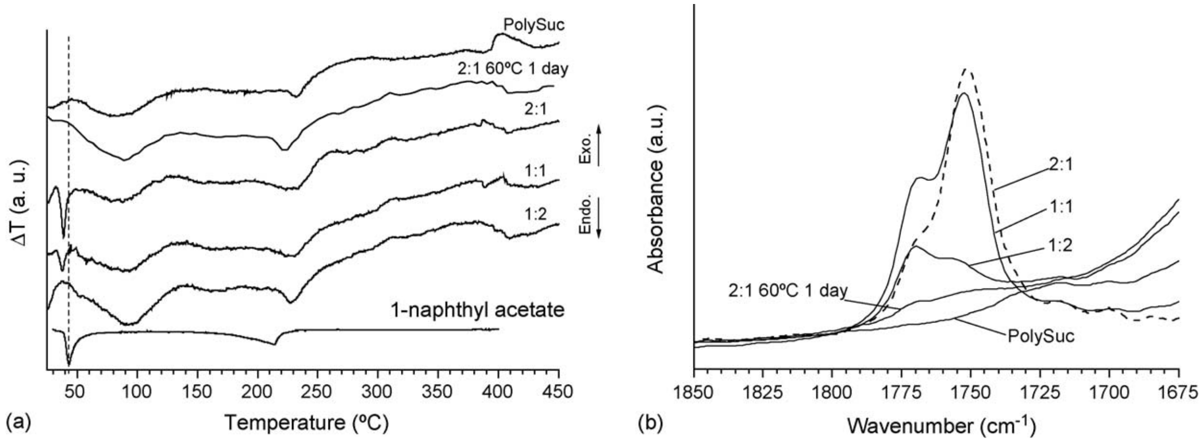


Fig. 7. (a) DTA curves of 1-naphthyl acetate:PolySuc mixtures; (b) FTIR spectra of 1-naphthyl acetate:PolySuc mixtures in the carbonyl stretching region.

systems and seems to be constant for the studied stoichiometries. For β-CD systems, the amounts of "associated" carbonyls are lower, and the 2:1 dispersion does not show the same shape as the two other stoichiometries. We showed that this fact supports the hypothesis of 1:1 complexes for these systems. In contrast, in the case of NA:Polyβ-CD, the similar infrared band shapes and thermal analysis results for the three dispersions indicate that NA:Polyβ-CD systems do not present a 1:1 stoichiometry. Inclusion within CD cavities is not the only mechanism of interaction to be considered in the case of Polyβ-CD: while an excess of 1-naphthyl acetate is easily lost from a β-CD dispersion by volatilization, for Polyβ-CD systems the sorbed amount can be higher than the corresponding 1:1 stoichiometric β-CD amount. Several authors have proposed that a 1:1 complex can bind to a second CD unit on the same polymer chain [20]. Moreover, Werner et al. [8] have pointed that a largely non-inclusional interaction, with a considerable participation of the glyceryl linker units, may be involved in the binding of pyrene to some CD polymers.

3.3. Sucrose polymer systems

Epichlorohydrin-linked sucrose polymers (prepared using sucrose instead of β-CD) are capable of sorbing aromatic molecules, as shown previously for other guest compounds [21]. The results for the sorption of naphthol and phenol into Polyβ-CD and PolySuc are displayed in Table 1. Both polymers present similar amounts of epichlorohydrin and apparent swelling in water although the water uptake is larger for Polyβ-CD. The affinity of 1-naphthol for both polymeric networks is higher than that of phenol. Polyβ-CD sorbs more of both aromatic compounds than the sucrose polymer, and the difference is higher in the case of naphthol. In order to study the stability of the naphthalene derivatives sorbed into the sucrose polymers, solid dispersions of 1-naphthyl acetate with PolySuc have been prepared (see Section 2). DTA results show that, in these mixtures, almost all the NA is in a crystalline form. As can be seen in Fig. 7(a), the endothermic melting peak of NA is intense for the 2:1 and 1:1 dispersions, but it is absent in the 1:2 dispersion. Nevertheless, the FTIR spectrum of the latter dispersion (Fig. 7(b)) demonstrates that NA is present at least in some extent. If the sample is heated at 60 °C, NA disappears in a few hours in all cases. The evaluated kinetics for this evolution (Fig. 5) shows that in 10 h the carbonyl peaks in the FTIR spectra were not appreciable for any of three molar ratios studied. The volatilization of NA in this case is the fastest of all the studied dispersions. Moreover, the shape of the carbonyl band for the 2:1 mixture was similar to that of pure NA, although a new contribution at higher wavenumbers can be detected in the other two dispersions (prepared with less NA). Thus, the shape of the 1:2 dispersion carbonyl peak was very similar to those of 1-naphthyl acetate:Polyβ-CD dispersions (Fig. 6). This could demonstrate a sorption in the sucrose polymer network, although the interaction is not as stable as that of the cyclodextrin polymer.

In previous works [13,18], we have shown that the disappearing of the out-of-plane bending C–H band of the aromatic moiety suggests a hindering due to a close fit to the cyclodextrin cavity. In Fig. 8, the spectra in the 500–950 cm^{-1} region shows how the band of 1-naphthyl acetate at 776 cm^{-1} is absent

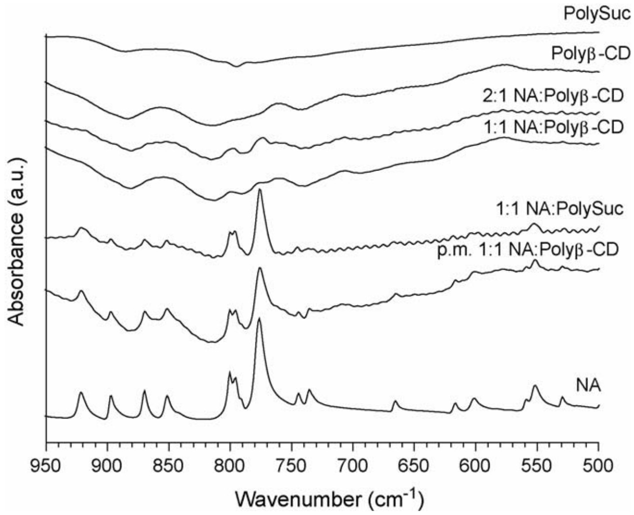


Fig. 8. FTIR spectra of 1-naphthyl acetate (NA) dispersions in the 950–500 cm^{-1} region. Spectra scaled using the NA band at 1600 cm^{-1} as the reference.

for NA:Polyβ-CD dispersions obtained by evaporation, while it is present in the PolySuc dispersions. Notice that the carbonyl bands of these dispersions (see Figs. 6 and 7) prove that NA has not been lost due to volatilization. This effect is also detected in 2-acetylnaphthalene and 1-naphthol for their respective aromatic C–H bands (835 and 765 cm^{-1}).

4. Conclusions

Although the main sorption mechanism of naphthalenes in Polyβ-CD is the inclusion within the CD cavities, the polymer network seems to confer an additional stability to the sorbed molecules when compared to monomeric β-cyclodextrin dispersions. Additionally, more aromatic moieties can be trapped within the Polyβ-CD network than the corresponding stoichiometric β-CD amount. Epichlorohydrin-linked sucrose polymers also sorb aromatic molecules, but cannot retain the naphthalene derivatives analyzed. In consequence, a synergic effect is found for β-cyclodextrin polymers: both the β-CD moieties and the network structures contribute to the higher amount of sorbed guest molecules and to their stabilization. Undoubtedly, the results of this investigation with model molecules will be of interest in the case of other guest molecules with various applications.

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References

[1] K.A. Connors, Chem. Rev. 97 (1997) 1325.
[2] A. Buvári-Barcza, A. Csámpai, L. Barcza, J. Incl. Phenom. Macrocycl. Chem. 42 (2002) 209.
[3] L. Liu, Q.X. Guo, J. Incl. Phenom. Macrocycl. Chem. 42 (2002) 1.
[4] J. Szejtli, T. Osa (Eds.), Comprehensive Supramolecular Chemistry, Cyclodextrins, 3, Pergamon, Oxford, 1996.
[5] G. Crini, M. Morcellet, J. Sep. Sci. 25 (2002) 789.
[6] (a) US Patent 4726905, 1988. American Maize Prod Co., invs.: R.B. Friedman, Y.R. West, Chem. Abstr. 107 (1989) 242412f;
(b) S. Murai, S. Imajo, Y. Maki, K. Takahashi, K. Hattori, J. Colloid Interface Sci. 183 (1996) 118;
(c) S. Murai, S. Imajo, Y. Takasu, K. Takahashi, K. Hattori, Environ. Sci. Technol. 32 (1998) 782;
(d) G. Crini, S. Bertini, G. Torri, A. Naggi, D. Sforzini, C. Vecchi, L. Janus, Y. Lekchiri, M. Morcellet, J. Appl. Polym. Sci. 68 (1998) 1973;
(e) F. Delval, G. Crini, N. Morin, J. Vebrel, S. Bertini, G. Torri, Dyes Pigments 53 (2002) 79;
(f) J.C. Yu, Z.T. Jiang, H.Y. Liu, J. Yu, L. Zhang, Anal. Chim. Acta 477 (2003) 93;
(g) X. Sevillano, A. Romo, J.R. Isasi, G. González-Gaitano, J. Peñas, in: D. Almorza (Ed.), Proceedings of the 1st International Conference on Waste Management and the Environment, Cádiz, Spain, September 4–6, WIT Press, Southampton, 2002, pp. 709–715.
[7] G. Crini, Bioresource Technol. 90 (2003) 193.
[8] T.C. Werner, K. Colwell, R.A. Agbaria, I.M. Warner, Appl. Spectrosc. 50 (1996) 511.
[9] F. Giordano, C. Novak, J.R. Moyano, Thermochim. Acta 380 (2001) 123.
[10] F. Trotta, M. Zanetti, G. Camino, Polym. Degrad. Stabil. 69 (2000) 373.
[11] V.T. Yilmaz, A. Karadağ, H. Içbudak, Thermochim. Acta 261 (1995) 107.
[12] G. Crini, C. Consentino, S. Bertini, A. Naggi, G. Torri, C. Vechhi, L. Janus, M. Morcellet, Carbohydr. Res. 308 (1998) 37.
[13] I.X. García-Zubiri, G. González-Gaitano, M. Sánchez, J.R. Isasi, J. Incl. Phenom. Macrocycl. Chem. 49 (2004) 291.
[14] OMNIC v. 5.1. Nicolet Instrument Corp., Madison, WI, USA.
[15] Microcal Origin TM. v. 5.0. Microcal Software Inc., Northampton, MA, USA.
[16] N. Goyenechea, M. Sánchez, I. Vélaz, C. Martín, C. Martínez-Ohárriz, A. Zornoza, J. Incl. Phenom. Macrocycl. Chem. 44 (2002) 283.
[17] K. Harata, H. Uedaira, Bull. Chem. Soc. Jpn. 48 (1975) 375.
[18] I.X. García-Zubiri, G. González-Gaitano, M. Sánchez, J.R. Isasi, Vib. Spectrosc. 33 (2003) 205.
[19] J.C. Netto-Ferreira, L.M. Ilharco, A.R. García, L.F. Vieira Ferreira, Langmuir 16 (2000) 10392.
[20] W. Xu, J.N. Demas, B.A. DeGraff, M. Whaley, J. Phys. Chem. 97 (1993) 6546.
[21] T.C. Werner, J.L. Iannacone, M.N. Amoo, J. Incl. Phenom. Macrocycl. Chem. 25 (1996) 77.