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Thermal analysis study of the interactions between acetaminophen and excipients in solid dosage forms and in some binary mixtures

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Abstract

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to assess the compatibility between acetaminophen (Ac) and some excipients (polyvinylpyrrolidone (P), magnesium stearate (M), citric acid (C), aspartame (As), mannitol (Mn), cellulose (Cll) and starch (S)) in several of the more commercially available pharmaceutical formulations and in solid binary mixtures. The present study compared thermodynamic data on acetaminophen melting and vaporization processes of pure acetaminophen with those found for several solid mixtures and in some commercially available acetaminophen-based dosage forms. Appreciable modifications occur only for solid mixtures with high content of excipient. Acetaminophen-based dosage forms and its solid binary mixtures usually show "additivity" of calorimetric peaks number of pure components in their calorimetric curve profiles, thus revealing a good thermoanalytical compatibility between acetaminophen and the excipients examined, except for samples containing appreciable content of mannitol.

Keywords: Acetaminophen; Thermal analysis; Dosage form; Compatibility; Excipients

1. Introduction

Assessment of possible incompatibility between active component (i.e. acetaminophen (Ac)) and different excipients along with the evaluation of thermal stability are crucial parts of the normal study prior to the final formulation setting of a solid dosage form [1]. Excipients are known to facilitate administration and release of an active component, as well as to protect it from the environment. Excipients are considered pharmaceutically inert but physical and chemical interactions with an active component are possible [2].

Isothermal stress testing and thermal analysis of pharmaceutical substances are routine methods for screening drug–excipient interactions. The latter has some advantages over the former as it requires only a few milligrams of sample per experiment and is not so time-consuming and expensive [2]. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used extensively to evaluate the physical properties of drugs, including melting and vaporization temperatures and with the corresponding enthalpies, glass transitions, vapor pressures, as well as to study the compatibility and stability of the components of pharmaceutical preparations [3–5]. In particular, DSC allows a rapid evaluation of possible incompatibilities by revealing changes in the appearance, shift or disappearance of melting or other exothermic processes, and/or variations in the corresponding enthalpies of reaction [6–8]. However, differences in the DSC curves of binary mixtures compared to the individual components may arise for reasons other than chemical incompatibility [9]. Sometimes, the presence of a solid–solid interaction may be advantageous, as in the case of a more desirable form of drug delivery system [10]. Therefore, DSC findings must be viewed with caution and in the case of substantial changes in DSC profiles of mixtures compared to

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that of the pure active component, complementary analytical techniques may be used to validate the interpretation of results [11].

Moreover, the water content due to humidity may affect the stability of active components, excipients and of finished products as well as the tableting properties of pharmaceutical formulations. In fact, tablets either crumble or cannot be obtained depending on whether the water content is too low or too high [3,6].

In the present study, the possible interactions between acetaminophen (in the most commonly available monoclinic form) and the tableting excipients (polyvinylpyrrolidone (P), magnesium stearate (M), citric acid (C), aspartame (As), mannitol (Mn), cellulose (Cll) and starch (S)), i.e. all the excipients contained in the examined dosage forms, have been evaluated. For this purpose, simultaneous TG/DSC measurements were carried out on each of the components, both in the pure form, in some of the corresponding solid binary mixtures Ac/excipient and in five commercial formulations containing Ac as active component. Thermodynamic and kinetic quantities related to the melting and subsequent vaporization (ΔH_{fus}, ΔH_{vap} and E_{vap}, respectively) were also determined for both pure Ac and for the five dosage forms. In order to assess the possible role of relative humidity (RH) in the considered dosage form stability considered, a DSC study was carried out on some components (Ac, C and As) under controlled humidity at room temperature.

2. Materials and methods

2.1. Materials and samples

Ac (lot 25322-118), M (lot 503492-203), As (39F0394) and S (type 20, S-3504) were supplied by Sigma–Aldrich; P (lot 436634-1), C (lot 62119793) and Cll (art. 1252) were obtained from Fluka and Merck, respectively, while Mn (lot 0531) was obtained from Carlo Erba. All the compounds were used as received without further purification. The composition of the pharmaceutical dosage forms tested, denoted as DF1–DF5, and the percentage of the active component contained (i.e. Ac) by weight, are displayed in Table 1. Physical binary mixtures of Ac and of C, P, M, As and Mn excipients were prepared in suitable proportions (80:20 and 20:80, w/w) by gently mixing them in an agate mortar with a spatula at room temperature. In addition, Ac and some excipients (i.e. C and As) were kept at $25 \pm 2\,^{\circ}C$ and at a controlled relative humidity of 55 ± 5 and $76 \pm 5\%$ for two months.

Table 1
Components in some of the examined commercially available analgesics (where Ac is always present as active component in large amount, except for DF5 dosage form)

Dosage forms	Ac content (%, w/w)	Contained excipients
DF1	94.1	Starch potatoes, Mg stearate, polyvinylpyrrolidone
DF2	87.5	Cellulose, Mg stearate, polyvinylpyrrolidone
DF3	83.6	Corn starch, stearic acid
DF4	85.1	Polyvinylpyrrolidone, Na carboxymethylcellulose, Mg stearate
DF5	35.5	Mannitol, aspartame, Mg stearate

2.2. Methods

The TG/DSC measurements of the individual components (both conditioned and not) as well as of mixed systems of Ac and excipients were carried out on a Stanton-Redcroft 625 simultaneous TG/DSC connected to a 386 IBM-compatible personal computer. Instrument calibration was performed using very pure standards. To this end, indium, gallium, lead, tin, naphthalene and benzoic acid samples were used in the present work as their temperatures and enthalpies of melting are well known.

Both for pure Ac and DF1–DF5 dosage forms, at least three rising temperature experiments were carried out in a temperature range from room temperature to 673 K while for all pure excipients, the scanning temperature range was from room temperature to 873 K. Different heating rates of 2.5, 5, 10 and 20 K min^{-1} were used during this study and at least three runs were performed for each heating rate. An open aluminium crucible was used to contain the sample and an identical empty aluminium crucible was used as reference material. A small sample weighing 4–6 mg, enough to uniformly cover the base of the crucible, was weighed out and placed in an argon-filled dry box to avoid oxidation of the sample. The simultaneous TG/DSC system was fluxed with the purge gas stream. In this way, the gases given off during the thermal heating process experiment were continuously removed.

Taking into account the sensitivity of our TG/DSC equipment, the vaporization of Ac (both in pure form and contained in DF1–DF5 dosage form samples) begins to be detectable after the completion of melting. For this reason, the kinetic calculations were performed for all the compounds in the molten state over the temperature range where the vaporization DTG curve is linear (before the sample reaches the DTG peak temperature).

The rate of a vaporization process ($d\alpha/dt$), as well as in the case of other thermally stimulated reactions, is expressed, as a function of the temperature, by the basic kinetic equation [12–14]

$$\frac{d\alpha}{dt} = k_{vap}(T) f(\alpha) \quad (1)$$

where t is the time, T the temperature, α the extent of conversion, and $f(\alpha)$ is the reaction model expressed by different mathematical expressions in relation with the mechanism of the transformation [12–14]. Moreover, vaporization kinetics, which is based on a constant area of reaction interface, is a zero-order process for which $f(\alpha) = 1$ [15]. The explicit temperature dependence [16] of the rate constant is introduced by replacing the k_{vap} vaporization coefficient with the Arrhenius

equation, which gives

$$\frac{d\alpha}{dt} = k_{vap}(T) = A \exp\left(\frac{-E_{vap}}{RT}\right) \quad (2)$$

and in the logarithmic form: $\ln k_{vap}(T) = \ln A - (E_{vap}/RT)$, where A and E_{vap} are the pre-exponential factor and the activation energy of vaporization, respectively. After a linear least square treatment of the $\ln k_{vap}$ data versus $1/T$, the activation energy of vaporization was obtained from the slope of the derived equation, R being the gas constant.

Finally, X-ray powder diffraction (XRPD) analysis was carried out on pure Ac as well as on solid binary mixtures Ac:excipient (80:20, w/w). For this purpose, a Philips diffractometer (PW 1130/00 model) using Ni filtered Cu Kα radiation (λ = 1.5141 Å) was used. The measurements of 2θ ranged between 5° and 50° (±0.05).

3. Results and discussion

The TG/DTG and DSC curves of DF1–DF5 Ac containing dosage form samples along with those of pure Ac are displayed in Fig. 1 while in Fig. 2, the TG/DTG and DSC curves of all the pure excipients contained in the studied dosage forms are compared with those of pure Ac. The trend of TG, DTG and DSC curves in Fig. 1 is almost identical for all the examined samples, with small differences for the DF2 dosage form. In the corresponding TG curve, a slight mass loss at the end of the main vaporization process is observed, to which corresponds a broad and not particularly intense thermal effect in the DSC curve. From the area of the corresponding DSC peaks, the enthalpies related to melting and subsequent vaporization (ΔH_{fus} and ΔH_{vap}) were determined, respectively, for both pure Ac and for Ac contained in the considered dosage forms at four different heating rates. Activation energies (E_{vap}) related to Ac vaporization were also determined according to a procedure [16] reported in Section 2.2. The results are shown in Table 2. By comparing the thermodynamic and kinetic values obtained for pure Ac and for Ac contained in the dosage forms tested, only a few differences were found, as shown in Table 2, i.e. ΔH_{vap} values for DF2 are slightly lower than those of pure Ac while ΔH_{fus} values are higher for DF5. The slight difference observed in sample DF2 is probably due to the presence of a small mass loss up to ≈600 K. This probably corresponds to the beginning of the decomposition of Cll, which is contained as excipient only in this dosage form. The higher ΔH_{fus} value for DF5 is probably due to interference of Mn, whose DSC peak of fusion is extremely close to that of Ac. Results obtained by considering Fig. 1 and Table 2 for all the other samples allow us to conclude that the small quantity of total excipients found in these drugs (5–15% by weight) does not significantly influence the thermal behaviour of the active component. In fact, the difference between ΔH_{vap} values in Ac and DF5 samples, probably due to the partial overlapping of decomposition process of Cll, is

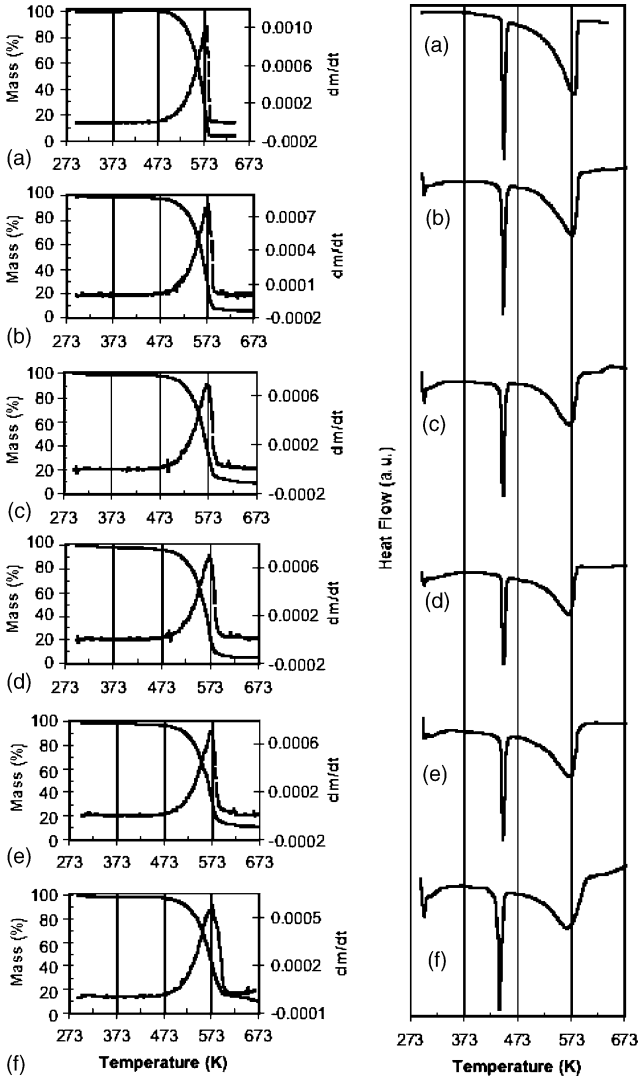

Fig. 1. TG, DTG curves (on the left) and DSC curves (on the right) of: (a) Ac, (b) DF1, (c) DF2, (d) DF3, (e) DF4, and (f) DF5, under a stream of argon (heating rate of 5 K min^{-1}).

very slight. However, for the DF5 sample, for which the total excipient content is higher (about 65% by weight), the difference with respect to the active component is particularly evident for the ΔH_{fus} value. This result is mainly ascribed to the superimposition of DSC peaks of fusion related to Mn and Ac.

In fact, TG, DTG and DSC curves in Fig. 2 show that in the range 445–610 K, only for C and Mn does almost the same thermal behaviour occur as for Ac. However, C melts over a slightly lower temperature range (431–450 K with respect to 447–469 K found for Ac). At higher temperatures, vaporization (without decomposition) occurs but the corresponding DSC peak (in a lower and narrower temperature range with respect to that of Ac) is observed at about 494.5 K instead of 600 K for Ac. On the other hand, Mn vaporization occurs at higher temperatures than that of Ac (about 638 K). Conversely, melting DSC peaks of both Mn and Ac are so close

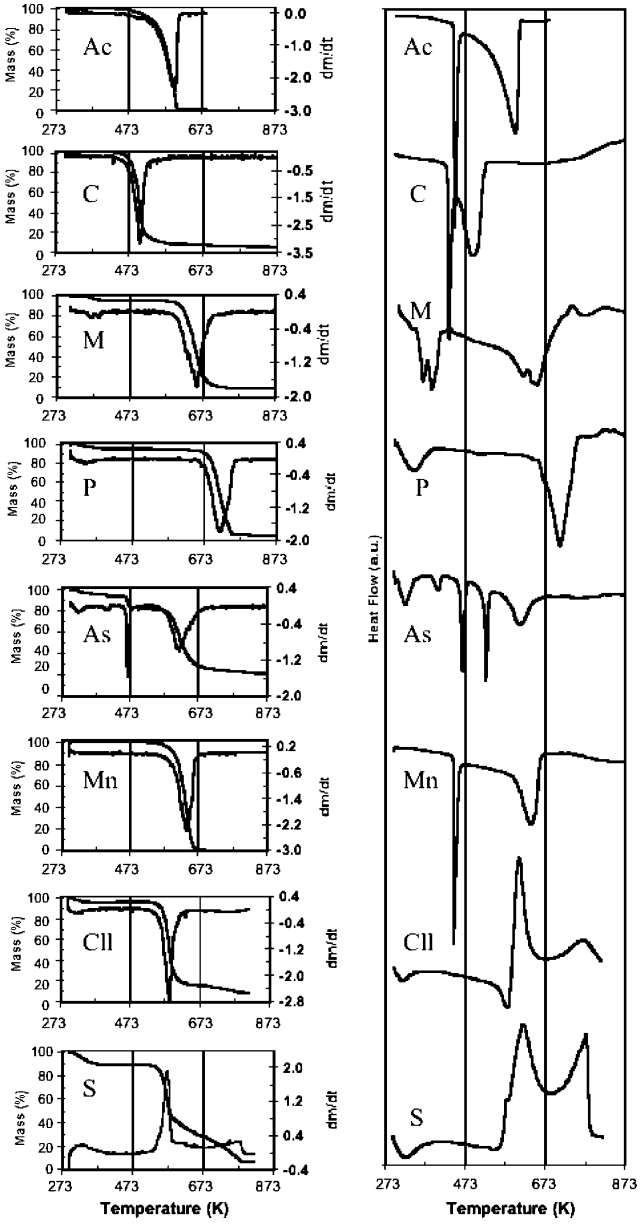

Fig. 2. Comparison of TG, DTG curves (on the left) and DSC curves (on the right) of all pure excipients of the considered dosage forms with those of pure Ac, under a stream of argon (heating rate of 5 K min^{-1}). Ac, acetaminophen; C, citric acid; P, polyvinylpyrrolidone; M, magnesium stearate; As, aspartame; Mn, mannitol; Cll, cellulose; S, starch.

that they can be considered almost superimposed (about 445 and 447 K, respectively). M and P show dehydration steps of mass loss under 430 K, followed by one or more decomposition steps over 600 K. Moreover, DSC peaks of As did not overlap with those of Ac and the content of As, usually contained in commercial drugs, is so low that no relevant thermal interferences can be detected. Lastly, after a slight water mass loss up to 373 K, Cll and S show decomposition processes above 565–570 K. Thus, these excipients do not affect the melting process of Ac at all, while they could probably partially affect the vaporization process of the latter. As

Table 2
Molar heats of fusion and of vaporization along with activation energies of vaporization both for pure Ac and for Ac in the dosage forms tested at different heating rates β

Compounds	β (K min^{-1})	ΔH_{fus} (kJ mol^{-1})	ΔH_{vap} (kJ mol^{-1})	E_{vap} (kJ mol^{-1})
Ac	2.5	22.4 ± 1.8	82.4 ± 2.8	86.8 ± 2.9
	5.0	21.9 ± 1.3	84.1 ± 3.0	85.3 ± 3.0
	10.0	22.8 ± 1.8	75.7 ± 3.0	86.0 ± 3.0
	20.0	24.0 ± 1.9	77.2 ± 2.8	85.6 ± 2.9
DF1	2.5	21.7 ± 1.7	84.2 ± 2.9	82.7 ± 3.0
	5.0	21.4 ± 1.7	84.9 ± 3.0	82.2 ± 3.0
	10.0	20.7 ± 1.6	78.0 ± 2.8	79.6 ± 2.8
	20.0	22.4 ± 1.9	75.5 ± 2.7	85.5 ± 3.0
DF2	2.5	17.8 ± 1.5	58.4 ± 3.0	84.4 ± 3.1
	5.0	20.1 ± 1.6	63.0 ± 3.0	85.9 ± 3.1
	10.0	20.2 ± 1.8	60.2 ± 3.0	83.0 ± 3.0
	20.0	19.5 ± 1.7	55.3 ± 2.9	80.7 ± 2.9
DF3	2.5	21.2 ± 1.5	83.0 ± 2.9	87.0 ± 3.0
	5.0	19.6 ± 1.4	71.7 ± 3.0	88.2 ± 3.0
	10.0	19.9 ± 1.4	70.4 ± 3.0	87.2 ± 3.0
	20.0	21.0 ± 1.6	69.3 ± 2.9	92.4 ± 3.2
DF4	2.5	17.3 ± 1.5	72.6 ± 2.9	77.7 ± 2.5
	5.0	19.0 ± 1.7	68.2 ± 2.7	81.0 ± 2.9
	10.0	19.5 ± 1.7	71.7 ± 2.6	82.3 ± 3.0
	20.0	17.4 ± 1.8	57.4 ± 2.4	76.3 ± 2.6
DF5	2.5	23.3 ± 2.3	74.9 ± 2.8	89.9 ± 3.0
	5.0	23.5 ± 2.1	75.5 ± 2.8	86.1 ± 3.0
	10.0	23.8 ± 2.2	67.7 ± 2.7	89.8 ± 3.0
	20.0	26.0 ± 3.6	62.3 ± 2.5	88.7 ± 3.0

already mentioned, this is effectively observed for the ΔH_{vap} value found for the DF2 dosage form.

In order to establish a possible interaction between Ac and some excipients that increase the percentage of the latter in solid dosage forms, some solid binary mixtures with different percentage ratio (by weight) Ac/excipient were prepared. To this end, samples of Ac (in the most commonly available monoclinic form) and of some of the main excipients (P, M, C, As, Mn) for which TG/DTG and DSC curves are shown in Fig. 2 were considered. Thus, in Fig. 3, the DSC curves obtained from the pure components and in some solid binary mixtures have been presented. For mixture samples with low content of excipient (Ac:excipient (80:20, w/w)) significant interference was found only in one case. Indeed, comparison of these curves indicates that, except for Ac:Mn (80:20, w/w) (as well as for DF5 dosage form samples), where only a single DSC peak (due to an overlapping of the two melting processes) is observed, a substantial additivity of "peak number" as well as of the peak shape with small or negligible differences in peak temperatures of pure components with respect to that of their binary mixtures is observed. Thus, no interaction occurs between the two components. Only when the excipient considered is the prevalent component, i.e. Ac:excipient (20:80, w/w), does the interaction become evident in the solid binary mixture. Indeed, in this case (Fig. 3), appreciable changes in both temperatures and profiles of melting as well as vapor-

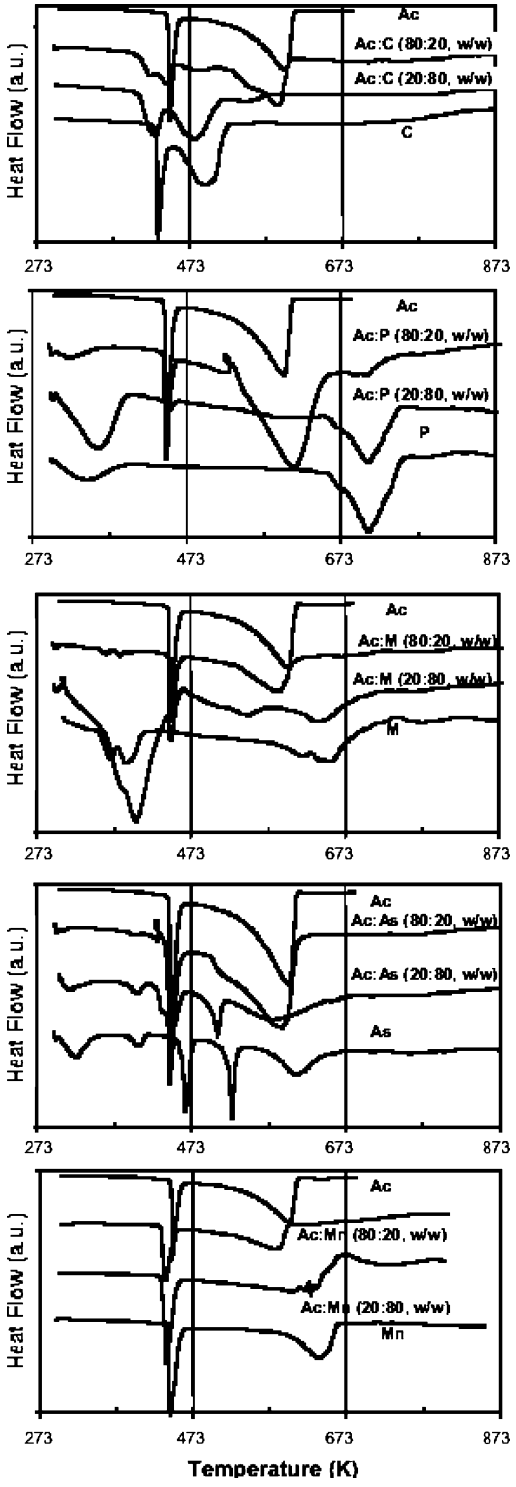

Fig. 3. DSC curves of the solid binary mixtures examined and of their pure components, under a stream of argon (heating rate of 5 K min^{-1}). Ac, acetaminophen; C, citric acid; P, polyvinylpyrrolidone; M, magnesium stearate; As, aspartame; Mn, mannitol.

ization DSC peaks were found for the Ac:excipient (20:80, w/w) samples with respect to those of pure Ac.

For further confirmation of a substantial compatibility between Ac and some of the excipients considered, XRPD spectra of Ac, as well as of the binary mixtures examined, Ac:excipient (80:20, w/w) were recorded and compared using the method proposed in [4]. The main structural effect of physically mixing two solid components (crystalline Ac and usually amorphous or at least poorly crystalline excipient) was, of course, to decrease the crystallinity of the mixture sample as indicated by a decrease in Ac peak intensities in the mixture (see Fig. 4). Moreover, almost all the peaks maintained the same position, except for the Ac peak at $2\theta \approx 45^\circ$ which is lost after the mixing treatment. As the properties of both the active component and the excipients, and the tableting properties of the pharmaceutical formulation, can be affected by the presence of water (moisture) [3,6], Ac and two excipients (C and As) were kept for two months at $25 \pm 2\,^\circ$C under a controlled relative humidity of 55 ± 5 and $76 \pm 5\%$, respectively. Then, onset temperatures of vaporization and melting enthalpies were determined from the TG and DSC curves, respectively. These experiments were carried out at 5 K min^{-1} for treated and untreated samples (the latter are

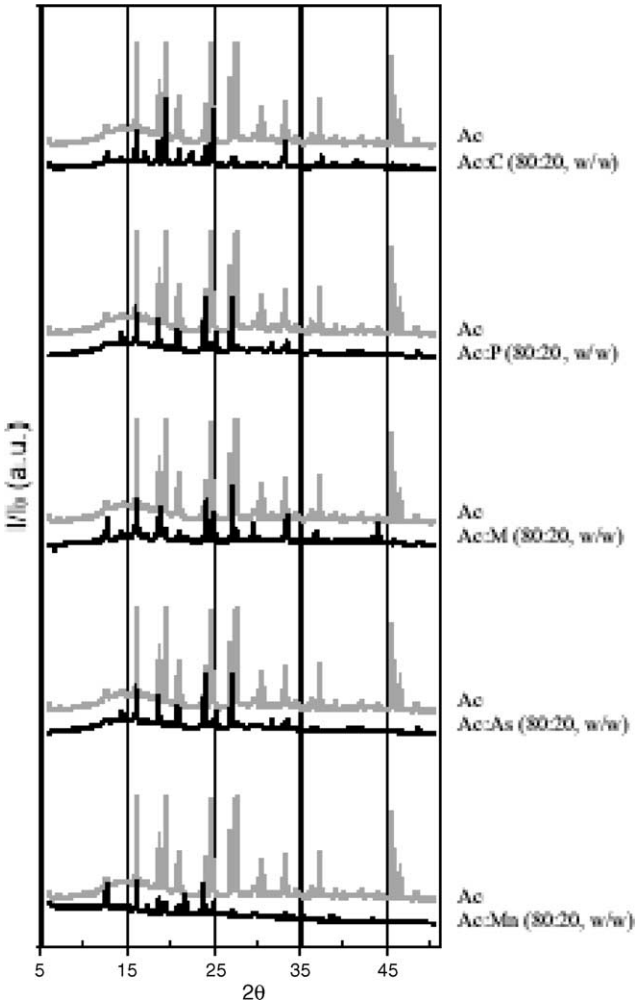

Fig. 4. XRPD pattern of pure Ac, and of the examined solid binary mixtures Ac:excipient (80:20, w/w) (Ni filtered Cu Kα radiation, λ = 1.541 Å). Ac, acetaminophen; C, citric acid; P, polyvinylpyrrolidone; M, magnesium stearate; As, aspartame; Mn, mannitol.

Table 3
Onset temperatures, melting temperatures and melting enthalpies for pure components both untreated and conditioned at fixed relative humidity for two months at 25 ± 2 °C, obtained from TG and DSC curves, respectively, carried out at 5 K min^{-1}

Components	t_{onset} (K)				t_{fus} (K)			ΔH_{fus} (kJ mol^{-1})		
	Step	NC	C 55%	C 76%	NC	C 55%	C 76%	NC	C 55%	C 76%
Ac	vap	566.1	560.3	556.5	447.6	447.6	447.2	22.8	23.5	24.6
C	vap	484.6	477.8	466.6	432.4	432.3	430.5	39.4	32.6	26.1
As	deh	312.4	279.8	299.1	–	–	–	–	–	–
	dec	396.2	395.4	400.7	–	–	–	–	–	–
	dec	460.9	460.1	460.1	–	–	–	–	–	–
	dec	592.8	591.2	592.1	–	–	–	–	–	–

vap represents vaporization processes, deh dehydration processes and dec decomposition processes. NC, not conditioned; C 55%, conditioned at a relative humidity of 55 ± 5%; C 76%, conditioned at a relative humidity of 76 ± 5%. The uncertainties were always less than 1 and 5% for temperatures and enthalpies, respectively.

shown in Fig. 3). The values obtained are summarized in Table 3. Onset temperatures of vaporization for Ac and C follow the expected decreasing trend. The same behaviour was observed for ΔH_{fus} values of C samples while that of Ac can be considered constant within the experimental error. Onset dehydration temperatures of As samples show an expected increasing trend with increasing ambient humidity of the two conditioned samples while an onset dehydration temperature higher than that expected is observed for the unconditioned sample. This behaviour is probably attributable to the uncontrolled degree of ambient humidity found for this kind of sample. Moreover, changes in the onset decomposition temperatures of As have to be considered as essentially lying within experimental error.

4. Conclusions

This compatibility study, mainly based on thermoanalytical methods, is qualitative in nature. The interest of the authors is to evaluate the experimental results in order to identify qualitative "compatibility-indicators", such as those obtained from the TG and DSC curves (temperatures, enthalpies and activation energies). From the present study, the following conclusions can be drawn:

1. By comparing thermal, thermodynamic and kinetic values for pure Ac and for Ac contained in the dosage forms, only slight differences are usually evidenced.
2. The only differences in thermal behaviour between pure Ac and the Ac contained in two of the examined dosage forms can be ascribed firstly to small mass losses at the higher temperature (around 610 K) observed for drug DF2, and secondly to the interference due to the simultaneous melting of Ac and Mn in the case of DF5 dosage form. Small differences in the vaporization enthalpies obtained at different heating rates are found for sample DF2 as well as clear differences in the melting enthalpies for sample DF5.
3. Changes in activation energies of vaporization found at different heating rates must essentially be considered to lie within experimental error (Table 2). This trend confirms that vaporization of Ac does not exhibit changes in the reaction mechanism [17] and is not substantially affected by other processes due to the presence of excipients in the pharmaceutical formulations.
4. For solid binary mixtures with low content of excipient (Ac:excipient (80:20, w/w)), a good compatibility was usually observed between Ac and the excipients tested (see additivity of DSC peaks number of pure components in its solid binary mixture), except for samples containing Mn as in the case of DF5 dosage form.
5. The same reasonable behaviour is also observed in the XRPD spectra of pure Ac compared to that of almost all the binary mixtures with low content of excipient (Ac:excipient (80:20, w/w)), thus demonstrating that no significant changes took place in the physical binary mixtures with respect to the chemical structure of the active component when this is the main component of the mixture. However, in all the mixtures, only one middle-intensity peak of pure Ac (around $2\theta = 45^\circ$) disappears and an appreciable decrease in peak intensity due to amorphization of the sample is observed. All these results reveal that only minor structural changes occur.

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