

THERMAL AND FTIR CHARACTERIZATION OF FILMS OBTAINED FROM CARBOPOL/SURFACTANT AQUEOUS SOLUTIONS

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Abstract

The suitability of differential scanning calorimetry (DSC) as a routine technique to characterize polymer/surfactant interactions in aqueous medium was evaluated in films obtained by evaporation of binary aqueous mixtures of Carbopol® 934, a cross-linked poly(acrylic acid), and Tween 80, Pluronic F-127 (non-ionic surfactants), sodium dodecylsulphate (SDS, anionic surfactant), or benzalkonium chloride (cationic surfactant). In all cases, the interactions that occur at specific proportions of both components, as shown in the FTIR spectra, could be detected by shifts of some melting peaks. Lorentzian deconvolution of carbopol carbonyl groups ($1690\text{--}1730\text{ cm}^{-1}$) was used to quantify the intensity of the interaction between the polymer and the non-ionic surfactants. DSC curves revealed the compatibility of carbopol with Tween 80 or SDS, and its strong affinity for Pluronic F-127 or benzalkonium chloride. This surfactant binds electrostatically to carbopol causing the formation of an insoluble polyelectrolyte complex, the composition and thermal behavior of which are very different from those of the films obtained from the supernatant.

Keywords: benzalkonium chloride, carbopol, carbopol/surfactant interactions, DSC, FTIR, Pluronic F-127, sodium dodecylsulphate, Tween 80

Introduction

The concomitant presence of both polymer and surfactant in an aqueous dispersion is receiving special attention since the formation of polymer/surfactant complexes can dramatically alter the properties of the system [1, 2]. Hydrophobic or electrostatic polymer/surfactant interactions can modify the viscosity and elasticity of polymer dispersions extraordinarily and can contribute to the stability/instability of multi-component mixtures [3]. Rheological data [4, 5] and adsorption isotherms [6] show that, in general, the relative proportions of the polymer and the surfactant govern the practical repercussions of their interactions. The surfactant begins to bind to the polymer at a critical aggregation concentration, *cac*, forming micelle-like aggregates

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along the polymer. Usually, *cac* is lower than the critical micellar concentration, *cmc*, of the surfactant, especially in the case of ionic surfactants in the presence of oppositely charged polymers. Between *cac* and *cmc*, the surfactant favors the interpolymeric interactions which result in the formation of a structured three-dimensional network, except when the surfactant and the polymer interact electrostatically which results in the precipitation of the system. Above *cmc* or the neutralization concentration, the surfactant will form micelles that can dissolve the complexes [7].

The aim of this study was to establish the suitability of the differential scanning calorimetry (DSC) of films as a routine technique to evaluate the interactions between Carbopol[®] 934, a slight cross-linked poly(acrylic acid) polymer commonly used in pharmaceutical preparations and technologic applications, and surfactants of different nature quickly. Very few DSC studies have been performed on polymer/surfactant mixtures [8] despite them being proved a useful technique for predicting polymer/polymer and polymer/drug interactions [9]. Films obtained from aqueous solutions are particularly adequate since the contact among their components is very close and their properties must reflect their interactions in liquid media. Films are also a convenient form for DSC analysis because they are easy to cut and fit to the bottom of the DSC pan, ensuring the best possible thermal contact. We have prepared films of carbopol/surfactant binary mixtures by evaporation of aqueous dispersions under mild conditions. Fourier transform infrared spectroscopy (FTIR) was used as a reference and complementary technique to interpret the results of the calorimetric analysis.

Experimental

Materials

Carbopol[®] 934NF (molecular mass 29400–39400 Da, batch AB17796) was provided by BFGoodrich Europe, UK. Benzalkonium chloride (batch 28H2518), sodium dodecylsulphate (SDS; batch 25H0537), poly(oxyethylene) 20 sorbitan monooleate (Tween 80; batch 90H0678) and poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) triblock copolymer (Pluronic F-127; batch 15H0651) were from Sigma. Purified water obtained by reverse osmosis (MilliQ[®], Millipore Spain) with resistivity <1.82 milli Ω cm was used.

Preparation of films

Aqueous dispersions of binary mixtures of carbopol-surfactant (Table 1) were prepared by mixing aqueous solutions of each component. The mixture was shaken for 2 h and then left to stand for 24 h at room temperature. To prepare the films, the dispersions were poured onto a Teflon plate and maintained at 40°C for 24 h. When a precipitate occurred, it was removed from the solution and dried under the same conditions as the supernatant. The samples will be referred to in the following sections as *Cn:Xm* where *C* represents carbopol, *X* the initial of the surfactant (i.e., F, T, SDS, or

B for Pluronic F-127, Tween 80, SDS, or benzalkonium chloride, respectively), and n and m the relative quantity of each component.

Table 1 Composition of carbopol/surfactant aqueous dispersions

Number	Carbopol/ mass/mass%	Surfactant/ mass/mass%	Polymer/surfactant mass ratio
1	1.00	0.00	6:0
2	0.84	0.16	5:1
3	0.66	0.33	4:2
4	0.50	0.50	3:3
5	0.33	0.66	2:4
6	0.16	0.84	1:5
7	0.00	1.00	0:6

Elemental analysis

C, N, O, and H content of carbopol/benzalkonium chloride films or aggregates was determined using a Carlo Erba 1108 elemental analyser (Italy).

DSC analysis

Known masses of film (1–2 mg) were sealed in 6 mm aluminium crucibles. DSC experiments were performed from 25 to 250°C at 10°C min⁻¹, in a Shimadzu DSC-50 apparatus (Japan) calibrated with indium (*m. p.*=156.6°C) and tin (*m. p.*=232.0°C).

Fourier transform infrared spectroscopy (FTIR)

Spectra were recorded by a FTIR Mattson ATR Spectra-Tech spectrometer (Germany) over the range 400–4000 cm⁻¹ using the ATR (attenuated total reflection) technique on a ZnSe crystal, except in the case of some carbopol/Tween 80 and carbopol/benzalkonium chloride mixtures for which it was necessary to prepare KBr disks. Lorentzian deconvolution of carbopol carbonyl groups was performed using a multi-peak curve fitting software (Microcal Origin 4.10, Northampton, MA). The hydrogen bonding percentage between carbopol and non-ionic surfactant was calculated using the following equation [10]:

$$H\% = [A_{1730} / (A_{1730} + A_{1700})] \cdot 100$$

where A_{1730} and A_{1700} are the area of the peaks at 1730±5 cm⁻¹ and at 1700±5 cm⁻¹, respectively.

Results and discussion

Carbopol/non-ionic surfactant films

DSC curves of carbopol/non-ionic surfactant films are shown in Fig. 1. Pure carbopol films (C6:T0 and C6:F0) only had a small endotherm around 100°C due to the evaporation of some remaining absorbed water, and another one close to 250°C that corresponds to the thermal decomposition process. Carbopol glass transition temperature, reported by Kanis *et al.* [9] at around 133°C, was not visualized. Pure Tween 80 film

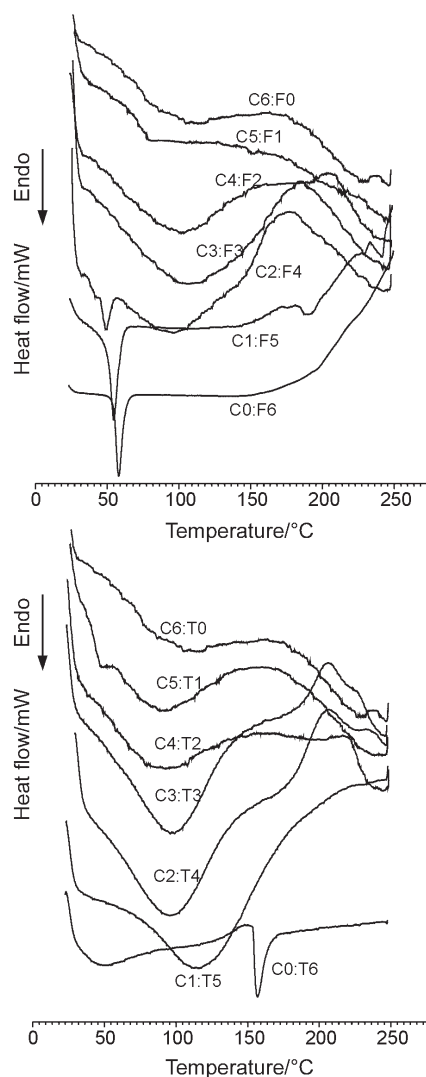


Fig. 1 DSC curves of carbopol: Pluronic F-127 (C:F) and carbopol:Tween 80 (C:T) films

(C0:T6) and pure Pluronic F-127 film (C0:F6) underwent endothermic flash point at 157°C and melting at around 58°C, respectively. These endothermic peaks shift to lower temperatures in the presence of carbopol (e.g., C1:T5 has a peak at 116°C, and C1:F5 at 53°C; Fig. 1), which is a clear indication of the polymer/surfactant miscibility and complex formation. It has previously been reported that the interaction of carbopol with non-ionic surfactants in water is usually weak except with ethoxylated surfactants such as Tween and Pluronic [11, 12]. In these systems, hydrogen bonding between the carboxylic groups of the polymer and the oxygen atoms of the surfactant chain promotes an aggregation process. It is also noticeable that in the case of carbo-

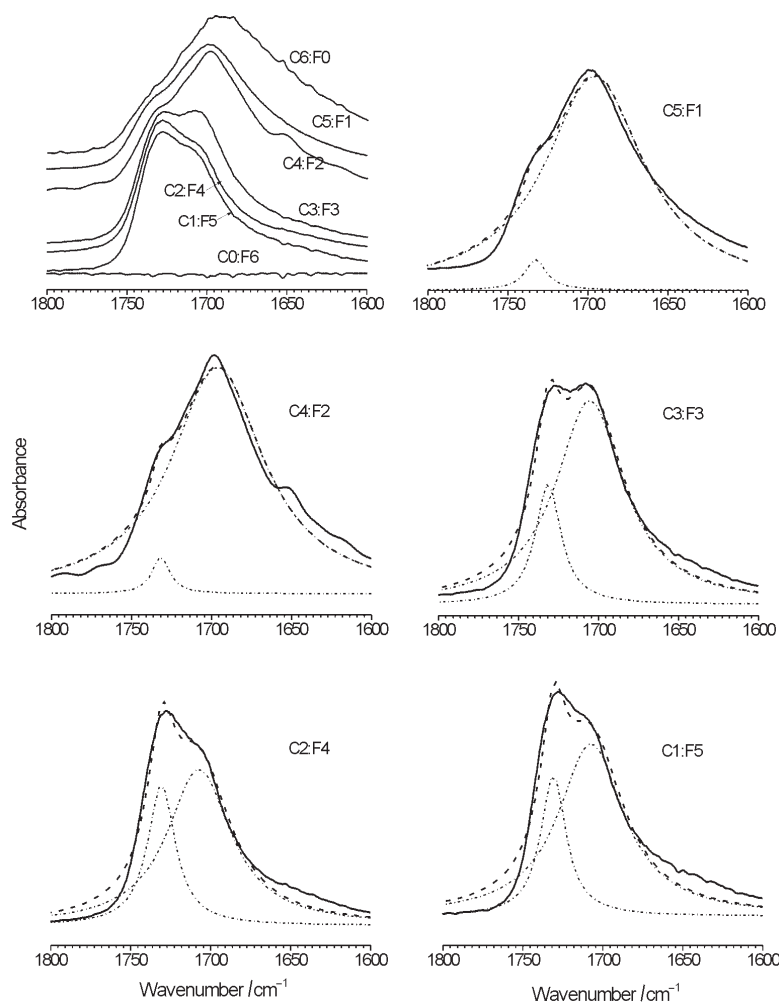


Fig. 2 FTIR spectra of carbopol:Pluronic F-127 films and their Lorentzian curve-fitting. The continuous line represents the absorbance observed; the bold dashed line, the absorbance simulated; the fine dashed lines, the simulated absorbances at 1700 and 1730 cm^{-1}

pol/Pluronic F-127 films, the enthalpy of fusion of Pluronic (-158 J g^{-1}) was much lower ($\Delta H_{C1:F5} = -88 \text{ J g}^{-1}$; $\Delta H_{C2:F4} = -5.5 \text{ J g}^{-1}$) than would be expected if the film were composed by non-interacting components in which the melting enthalpy is an additive property. The reduction in heat of fusion is usually interpreted as interaction between the components [13]. In our case, it may be interpreted as carbopol/poloxamer aggregation since during the mixing of the dispersions for preparing the films an intense cloudiness was observed, which already suggested an intense complex formation. Films were prepared by mixing solutions of carbopol and each surfactant. Each component was previously completely dissolved separately, and in all cases the viscosity of each solution was quite low. Therefore, the cloudiness of some carbopol/Pluronic mixed solution can't be attributed to a limiting mixing or to crystallization.

This interaction phenomenon is clearly shown in the FTIR spectra shift of the carbonyl stretch of carbopol. The infrared spectrum of carbopol is characterized by a broad band of carbonyl stretch of the carboxylic group at 1700 cm^{-1} [14]. The broadening of this band is attributed to the existence of two carbonyl populations, one corresponding to the intra- and intermolecular hydrogen bonding and another due to free carbonyl groups (Fig. 2). This band moves to a higher vibration frequency (1730 cm^{-1}) with the increase of non-ionic surfactant, indicating the diminution of the internal hydrogen bonding of carbopol and the formation of new bonds with the surfactant [9, 15]. To estimate the percentage of hydrogen bonding with the non-ionic surfactant, the band was deconvoluted in two peaks by Lorentzian curve-fitting, and the ratio of the areas of 1730 and 1700 cm^{-1} was calculated (Table 2). For both surfactants, the hydrogen bonding with carbopol increased continuously with the addition of surfactant and reached a maximum for carbopol:surfactant proportion 2:4. The higher hydrogen bonding values observed with Tween 80 may be attributed to its smaller molecular size compared to Pluronic F-127, which provides for an equal mass proportion, more molecules that can penetrate the carbopol microgels easily.

Table 2 Hydrogen bonding percentage between carbopol and Pluronic F-127 or Tween 80 calculated by Lorentzian multi-peak fitting [9]

Composition	Components ratio/ mass/mass	H%
Carbopol/Pluronic F-127	5:1	2.33
	4:2	2.99
	3:3	18.0
	2:4	28.0
	1:5	23.9
Carbopol/Tween 80	5:1	4.22
	4:2	9.25
	3:3	18.6
	2:4	64.5
	1:5	48.7

Carbopol/anionic surfactant films

DSC curves of pure SDS showed two characteristic endothermic peaks (Fig. 3); one at 105°C, which might correspond to the vaporization of adsorbed water or organic alcohols that are a common impurity of commercial SDS, and a second one at 193°C due to the melting process of the surfactant [8, 16]. Its interaction with carbopol is suggested by the decrease in the melting temperature of the surfactant, the peak of which is transformed into two when carbopol concentration increases, although the

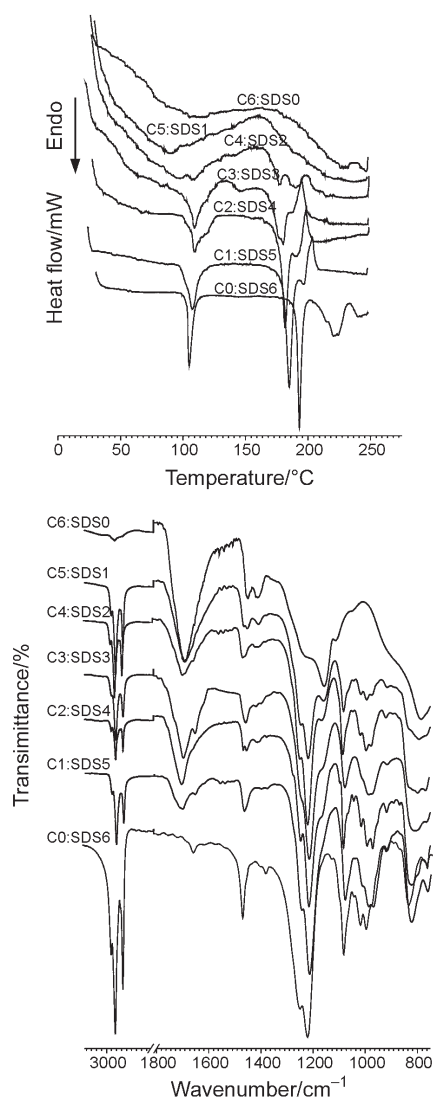


Fig. 3 DSC curves and FTIR spectra of carbopol:SDS films

heat of fusion remained unaltered. For example, C4:SDS2 films presented a peak at 175 and another one at 189°C, close to pure SDS, which might indicate the existence of two phases, i.e. one formed by a polymer-surfactant complex and another one by free surfactant. FTIR spectra of the films (Fig. 3) exhibited the characteristic band of

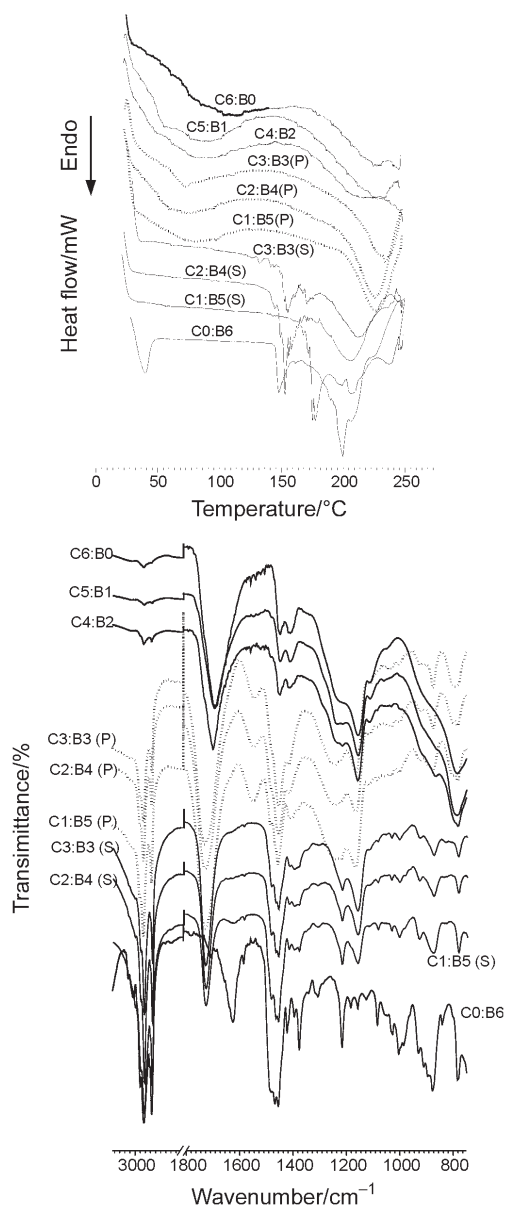


Fig. 4 DSC curves and FTIR spectra of carbopol: benzalkonium chloride films. When precipitation (P) occurred, the spectra were recorded using KBr tablets

SO_3^{2-} stretching vibration at 1210–1250 cm^{-1} [17] and slight shifts in the carbonyl groups band of carbopol, much less important than in the case of the non-ionic surfactants. These observations suggest that, although carbopol and SDS are compatible in the whole range of proportions, a weak hydrophobic polymer/surfactant interaction occurs, as was previously reported for poly(acrylic acid)s and anionic surfactants [6].

Carbopol/cationic surfactant films

The addition of benzalkonium chloride, in proportions equal to or above the amount of carbopol, to the polymer solution caused the formation of a precipitate. In these cases, the precipitate was removed from the solution, dried under the same conditions as the supernatant, and analyzed separately. DSC curves showed a very different behavior between the precipitate and the film obtained by evaporation of the supernatant (Fig. 4). The sample of the precipitate had a pattern similar to pure carbopol except for the broad band that appeared at 234°C in the C3:B3 mixtures and was gradually shifted to 227°C in the C1:B5, which may be related to the decomposition of pure benzalkonium chloride (197°C). In contrast, in the case of the supernatant films, this broad band appeared at a temperature (212–206°C) closer to the pure surfactant and, in addition, new intense peaks emerged at 153–178°C, which may correspond to the melting of free and bound surfactant molecules. Pure benzalkonium chloride develops a melting process at 148°C. These results suggest that carbopol is the main component in the precipitate, while benzalkonium chloride is predominant in the supernatant where there are both free and bound surfactant molecules. Benzalkonium chloride can interact electrostatically with the carboxylic groups of carbopol by displacing the protons. The apparition of the ionized carboxylic groups band (1540 cm^{-1}) in the FTIR spectra of the precipitates (Fig. 4) clearly proves the formation of polyelectrolyte complexes [18]. This band is much less evident in the supernatant, in which the bands of the surfactant become more intense. The difference in composition between the precipitate and the films of the supernatant was also confirmed by elemental analysis. The precipitate has in all cases an almost constant composition of equal amounts of carbopol and benzalkonium chloride, equivalent to 5:1 carboxylic:ammonium groups mole ratio. In contrast, as predicted by DSC, the amount of surfactant was higher in the supernatant and increased gradually as more surfactant was added during preparation of the blends.

Conclusions

The results obtained in the characterization of carbopol/surfactant films proved the suitability of DSC as a useful technique for a quick characterization of polymer/surfactant interactions and even for the approximate estimation of the composition of each phase when a precipitation occurs. In addition, DSC provides supplementary information to that obtained using more complex analytical techniques.

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