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Complexation (cucurbit[6]uril-pyrene): Thermodynamic and spectroscopic properties

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ABSTRACT

The influence of the macrocyclic compound cucurbit[6]uril (CB6) on the photophysical properties of the fluorophore pyrene (PYR) has been studied. Guest–host interaction was observed by UV–visible spectroscopy and spectrofluorimetry. The fluorescence of PYR was significantly increased in the presence of CB6. The binding equilibrium constants for the complex with 1:1 stoichiometry were determined in HCOOH 55% w/v. The values of the association constants, K_A, and the fluorescence quantum yield ratios between complexed and free substrate, $\phi^{PYR-CB6}/\phi^{PYR}$, at different temperatures were $(3.1 \pm 0.9) \times 10^2\ M^{-1}$ and (5.1 ± 0.2), $(3.6 \pm 0.5) \times 10^2\ M^{-1}$ and (5.9 ± 0.1), $(4.8 \pm 0.7) \times 10^2\ M^{-1}$ and (5.5 ± 0.1) at 15.0 °C, 25.0 °C and 40.0 °C, respectively.

The enthalpic and entropic contributions to the complexation process were determined, yielding $\Delta S = (92 \pm 3)$ J mol^{-1} K^{-1} and $\Delta H = (13 \pm 1)$ kJ mol^{-1}. From these results it can be concluded that the complex formation is mainly driven by the entropic term. The forces involved in the complexation are interpreted from the sign and magnitude of the thermodynamic parameters obtained.

The partial inclusion of PYR or the formation of a suspended complex is proposed in base of all the data. The interaction is also demonstrated in the solid state by differential scanning calorimetric (DSC) measurements.

1. Introduction

Cucurbiturils are a class of macrocyclic oligomers constituted by glycoluril units linked by a pair of methylene bridges that define a highly rigid and symmetrical structure with a hydrophobic cavity and two identical portals surrounded by carbonyl groups [1]. The photophysical properties of several fluorophores could be modified by complexation with these supramolecular receptors [2,3].

The fluorescent intensities of the dye curcumin and the benzoimidazolic fungicide carbendazim is increased by association with cucurbit[6]uril [4,5]. The homolog cucurbit[7]uril also induces the fluorescence enhancement of the natural isoquinoline alkaloids berberine [6] and coptisine [7] and the dicationic 2,7-dimethyldiazapyrenium [8]. The formation of the exclusion complexes between thioflavin T and CB5 [9] and between riboflavin and CB7 [10] modifies the photophysical parameters of these fluorescent compounds.

The heptamer homolog modifies the luminescent properties of various fluorescent probes, as 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) [11,12], 2-anilinonaphthalene-6-sulfonate (2,6-ANS) and 1-anilinonaphthalene-8-sulfonate (1,8-ANS) [13]. The improvement of the quantum yields of 2,6-ANS and 1,8-ANS was attributed to the formation of 1:1 inclusion and 1:2 exclusion, sandwiched type, complexes, respectively [13]. The emission intensities of 2,6-ANS also increased by interaction with CB6 [14] whereas the addition of this macrocycle to a 1,8-ANS solution induces the formation of a fluorescent solid complex [15].

The formation of 1:1 inclusion complexes of several cationic fluorescent dyes, as rhodamine 6G, rhodamine B, acridine red, acridine orange, brilliant green, 4′,6-diamidino-2-phenylindole, 3,3′-diethylthiacarbocyanine iodide, thioflavin T, with CB7 induces spectral shifts and the change of the fluorescence quantum yields, brightness, fluorescence lifetime and photostability of these fluorophores [2,3,16,17]. Whereas CB7 prevents the aggregation of tricyclic basic dyes, CB8 encapsulates two or three of these molecules reducing their fluorescent signals [18]. The intensification of the excimeric band of thioflavin T in the presence of CB8 was related to the formation of a 2:2 complex [19]. The 2,4,6-triphenylpyrylium cation and CB8 form a phosphorescent complex at room temperature [20].

In the field of supramolecular analytical chemistry [21], we have previously proposed the applicability of CB6 as nanosensor for determining pyrene by developing an alternative analytical

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method based on enhanced fluorescence spectroscopy at room temperature of the polycyclic aromatic hydrocarbon in presence of this macrocycle [22]. The application of the proposed method was demonstrated in spiked samples of tap water and tea with very good recoveries [22].

The interaction between CBn and cationic guest has been much more explored and interpreted than with neutral compounds. Thereby, the aims of this work is study the effect of CB6 on absorption and fluorescence spectra of the neutral polycyclic aromatic hydrocarbon pyrene and estimate the thermodynamic parameters to assess the nature of the forces involved in this guest–host complexation. Additionally, an evidence of the interaction in the solid state is demonstrated by differential scanning calorimetric (DSC) measurements.

2. Material and methods

2.1. Apparatus

The UV–visible measurements were registered with a Shimadzu UV-2101PC or a Shimadzu MultiSpec-1501 with diode array detection (Kyoto, Japan) instruments employing a 1 cm quartz cell. The spectrofluorimetric determinations were carried out in a Jasco FP-777 (Tokyo, Japan) spectrofluorometer. An ultrasonic bath Testlab tb02 (Bernal, Buenos Aires, Argentina) was used for solubilizing the samples. Data analysis was performed with SigmaPlot (Scientific Graph System) Version 10.0 (Systat Software Inc.). NMR spectra were recorded on a Bruker AC (200 MHz) or a Bruker Avance II (400 MHz) instrument. ESI/MS was done in a Varian 1200-Q III Spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) curves were acquired on a MDSC 2920 TA apparatus under dry nitrogen purge gas flowing at 50 mL min^{-1}. Samples were placed in hermetically-sealed aluminum pans and heated at constant scanning rate of 10 °C min^{-1} in the range 50–550 °C.

2.2. Reagents

The water was obtained from a Milli-Q water purification system. Glycoluril (Aldrich) and formaldehyde solution (36% in water, Fluka) were used as received. Pyrene (98% purity, Aldrich) was purified by sublimation. Methanol was HPLC grade (Sintorgan, Villa Martinelli, Buenos Aires, Argentina). Formic and hydrochloric acids were analytical grade (Cicarelli, San Lorenzo, Santa Fe, Argentina). The NMR samples were prepared using a (1:0.75) mixture of DCl (35% w/w, Aldrich) and D_2O (Aldrich) as solvent. The signal of this solvent, previously calibrated with 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP, Aldrich), was used as an internal reference.

2.3. Synthesis of cucurbit[6]uril

Cucurbit[6]uril was synthesized from glycoluril and formaldehyde according to the method described in literature [23–25] with some modifications in the separation and purification procedures to yield a product with optimal properties for spectroscopic studies [26]. The hydrochloric acid was employed in the synthesis with the purpose to obtain the reaction mixture without colored impurities and, consequently, a white solid product. The use of methanol and water provides an optimal method for the purification and isolation of this macrocycle. CB6 was characterized by NMR spectroscopy and electrospray ionization mass spectrometry.

A mixture of glycoluril (10.79 g, 76 mmol) and concentrated hydrochloric acid (60 mL) was stirred at room temperature and for 30 min, then formaldehyde (12 mL, 160 mmol) was added and heated with stirring for 27 h at 116 °C. The resulting reaction mixture was cooled to room temperature and poured into a mixture of CH_3OH/H_2O 5:1 v/v (1200 mL) placed in an ice bath forming a white precipitate that was isolated by filtration with suction and recrystallized with a mixture of CH_3OH/H_2O 1:2 v/v (200 mL). The precipitate was filtered with vacuum newly, recrystallized and washed with water several times. The recrystallizations in water eliminate the CB5 and CB7 homolog's due to their higher solubility in this solvent. The white solid was collected by filtration and vacuum dried until constant weight was reached (9.49 g; 75.3% yield). ^{1}H NMR (400 MHz, DCl/D_2O 1/0.75): δ 4.40 (d, 12H, J=15.5 Hz), δ 5.60 (d, 12H, J=15.5 Hz), δ 5.64 (s, 12H). ^{13}C NMR (400 MHz) δ 49.5, 69.2, 154.6. ESI-MS (higher relative intensities, %): m/z 1019 $[CB6+Na]^+$ 100%, 996 $[CB6]^+$ 96.5%, 1072 $[CB6+3H_2O+Na]^+$ 93.6%, 997 $[CB6+H]^+$ 53.5%, other six CB6 adducts were observed with a total of relative intensities of 240%, only two CB5 adducts were observed with minor relative intensities (853 $[CB5+Na]^+$ 12.2% and 869 $[CB5+K]^+$ 36%. These characterizations are consistent with literature data [24,25].

2.4. General methods

A concentrated solution of PYR in methanol (10 mg per 25 mL) was prepared. This solution was stored at 4 °C and checked by spectrophotometry before preparing the diluted solutions for fluorimetric determinations.

The solubility of the synthesized CB6 was assessed in order to choose the medium in which the experiments would be performed. The tests were carried out adding gradually 0.1 mL aliquots of the evaluated solvent to 15 mg of CB6 previously weighed until the solid was completely solubilized or until 3 mL of solvent were added. Between each addition, the container was placed approximately 10 min in an ultrasonic bath at 35 °C. The amount used of the macrocycle was not completely solubilized in aqueous solution of sodium chloride ([NaCl]=0.4 M), potassium chloride ([KCl]=0.4 M), sodium sulfate ($[Na_2SO_4]$=0.2 M) and ammonium acetate ($[CH_3COONH_4]$= 1 M). These observations are consistent with the results reported by some authors [27], although others inform higher values of solubility [28]. Conversely, it was possible to prepare solutions with the desired maximum concentration (50 mM) using aqueous HCOOH 55% (w/v), as it was reported in the literature [29,30].

For the determination of the binding constant values, solutions with different concentrations of CB6 (0–44 mM) were prepared mixing two solutions with the same PYR concentration (one without CB6 and the other with the maximum concentration of CB6 used) in order to minimize the changes by variations in the substrate concentration. In both, acid percent (HCOOH 55% w/v) and CH_3OH (2% v/v in spectrophotometric determinations and 1% v/v in spectrofluorimetric determinations) were kept constant. The concentration of PYR employed in spectrophotometry and spectrofluorimetry were 11.8 μM and 0.215 μM, respectively. The acidic media were necessary for CB6 solubilization. The calibration curve of CB6 was determined subtracting the acid media signal. The solutions were not degassed and were wrapped with aluminum foil.

The fluorescence emission spectra were registered with the excitation wavelength corresponding to the isosbestic point between the free and the complexed substrate (λ_{ex}=335 nm). The absorption for the highest concentration of CB6 at this wavelength was lower than 0.08 (path length=1 cm). The photomultiplier gain was high and the emission and excitation bandwidths were set at 3.0 nm and 1.5 nm, respectively. A 0.30 cm × 0.30 cm quartz cell was used. A solution of 0.215 μM of PYR at pH=7.00 (CH_3OH 1% v/v) was used as reference. In all cases, the total area below the fluorescence spectrum (F) was measured. The determinations were carried out at 15.0 ± 0.1 °C, 25.0 ± 0.1 °C and 38.0 ± 0.1 °C. The temperature of the cell compartment was controlled with a Haake circulator.

2.5. Synthesis of the solid complex

A sample of 48 mg of PYR in 10 mL of CH_3OH was poured into a sample of 255 mg of CB6 (equimolar ratio to the PYR) producing a white precipitate. The mixture was heated at 50 °C with stirring for 12 h and then was filtered using a nylon membrane of 0.2 μm pore size. The solid obtained was vacuum dried until constant weight was reached.

3. Results and discussion

3.1. Effect of CB6 on the spectrophotometric properties of PYR

The maxima of the UV–visible spectrum of PYR showed slight variations in the absorbance in the presence of the macrocyclic receptor (Fig. 1). The difference spectrum between a solution of PYR with a maximum CB6 concentration used (38.8 mM) and one without it (not shown) presents the maximum absorbance difference at 320.0 nm ($\Delta A_{max}=0.057$ with path length = 1 cm).

Based on literature data [31], these spectral changes could be attributed to the complex formation between the substrate (PYR) and the host (CB6) according to the following (1)

$$PYR + CB6 \overset{K_A}{\rightleftharpoons} PYR\text{–}CB6 \quad (1)$$

The changes in absorbance with increasing concentrations of CB6 were measured at 320.0 nm (Fig. 2A). The binding constant (K_A) for the 1:1 complex was determined from non-linear fitting of the data to Eq. (2), where A is the total absorbance in the presence of CB6 and A_0 is the absorbance of the solution without the host and b is the path length of the sample.

$$A = A_0 + \frac{b\ \Delta\varepsilon_{PYR-CB6}\ [PYR]_0\ K_A\ [CB6]_0}{1\ +\ K_A\ [CB6]_0} \quad (2)$$

The value of K_A was $(4 \pm 1) \times 10^2\ M^{-1}$. Furthermore, the 1:1 stoichiometric ratio was confirmed fitting the data according to a linearized equation derived from Eq. (2) (Fig. 2B) [31].

3.2. Effect of CB6 on the fluorescence of PYR

The fluorescence emission spectrum of PYR in the acidic media ([PYR] = 0.215 μM; CH_3OH 1% v/v; HCOOH 55% w/v; 25.0 °C; λ_{ex} = = 335 nm) presents five characteristic vibronic bands with maxima at: 373.5 nm, 377.5 nm, 384.0 nm, 388.0 nm and 394.0 nm, which are numbered from I to V according to the increasing order of wavelength [32]. The ratios between the intensities of the bands III and I ($R_{III/I}$) and the peaks V and I ($R_{V/I}$) increase gradually from 0.58 to 0.77 (Fig. 3) and from 0.78 to 0.89, respectively, with the increment of the percentage of methanol.

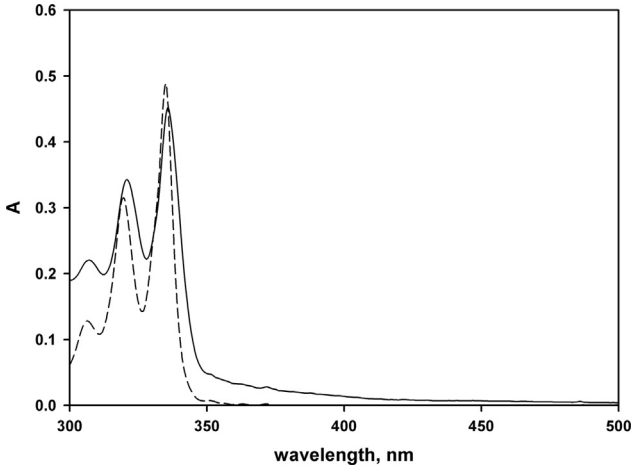

Fig. 1. UV–visible spectra of PYR in absence and in presence of CB6 ([PYR] = 11.8 μM; [CB6] = 38.8 mM; CH_3OH 2% v/v; HCOOH 55% w/v; 25.0 °C; b = 1 cm).

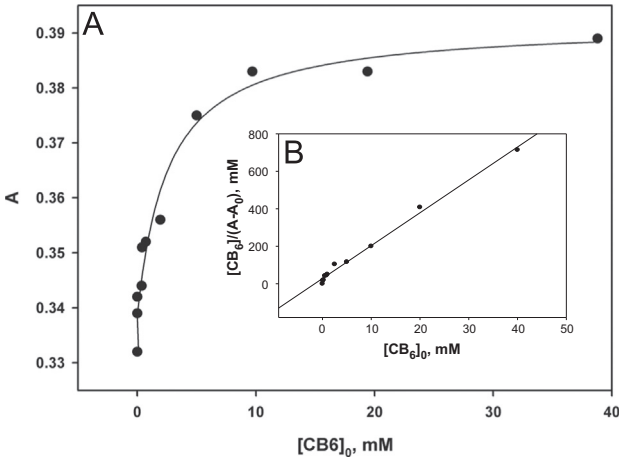

Fig. 2. Absorbances at 320.0 nm of PYR as a function of CB6 concentration ([PYR] = 11.8 μM and 25.0 °C). (A) Non-linear plot (the solid line shows the best fit of the data to Eq. 2). (B) Linear double reciprocal plot according to a linearized equation in Refs. [25].

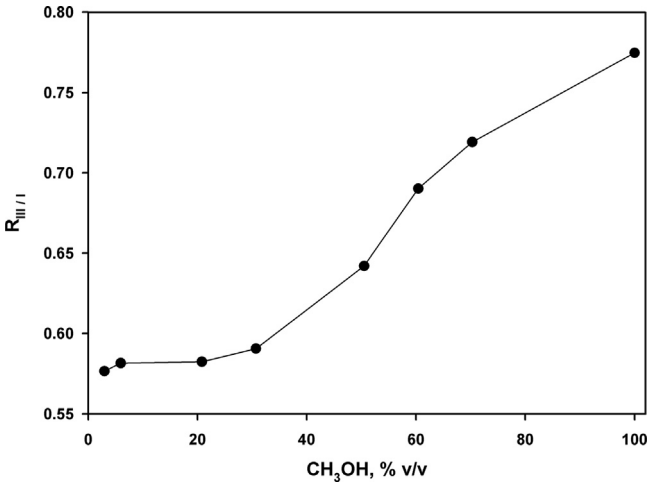

Fig. 3. Effect of the variation of the percentage of methanol on the relative fluorescence intensity of aqueous solutions of PYR ([PYR = 0.109 μM). The solid line joins the experimental data points.

In the presence of CB6, the fluorescence emission spectrum of the aromatic compound displays a pronounced enhancement (Fig. 4). Whereas the addition of glycoluril (weight equivalent to the quantity used for CB6) had no effect on the fluorescent signals, indicating that the spectral changes observed with CB6 are related to specific interactions between the substrate and the macrocyclic compound. The unstructured band centered at 460.0 nm, which is associated with the pyrene excimer formation, was not observed in the fluorescence emission spectra [33].

Interestingly, the addition of the macrocycle also induces the increase of the intensities ratios between the vibronic bands III and I, $R_{III/I}$ (from 0.57 without CB6 to 0.63 with CB6) and $R_{V/I}$ (from 0.76 without CB6 to 0.89 with CB6) suggesting that the luminophore is located in a less polar environment with respect to the bulk of the aqueous solution. A similar effect on the relative intensities of PYR by addition of CD was described in the literature [34].

The variation of the fluorescence as a function of CB6 concentration is given by Eq. (3), where F and F_0 represent the total fluorescence in the presence and absence of the macrocycle, respectively; K_A is the binding constant previously defined and

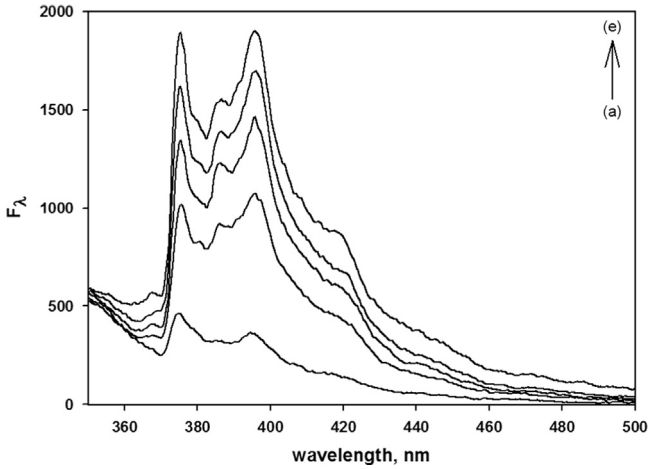

Fig. 4. Fluorescence emission spectra of PYR at different concentrations of CB6: (a) 0 mM; (b) 1.89 mM; (c) 7.56 mM; (d) 15.1 mM and (e) 37.8 mM ([PYR]= 0.215 μM; CH_3OH 1% v/v; HCOOH 55% w/v; 25.0 °C; λ_{ex}=335 nm).

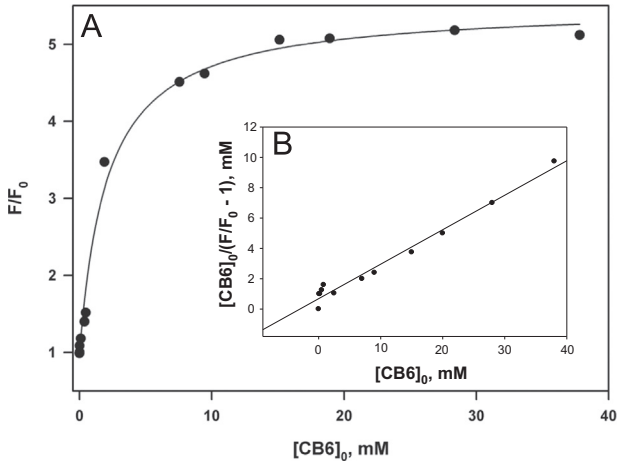

Fig. 5. Dependence of the relative fluorescence of PYR with the CB6 concentration ([PYR]=0.215 μM and 40.0 °C). (A) Non-linear plot (the solid line shows the best fit of the data to Eq. (3)). (B) Linear double reciprocal plot according to a linearized equation. The relative error in fluorescence experimental values was ±5%.

Table 1
Association constants (K_A) and fluorescence quantum yield ratios at different temperatures [a].

Temperature (K)	K_A ($\times 10^2$ M^{-1})	$\phi^{PYR-CB6}/\phi^{PYR}$
288	3.1 ± 0.9	5.1 ± 0.2
298	3.6 ± 0.5 [b]	5.9 ± 0.1 [b]
315	4.8 ± 0.7	5.5 ± 0.1

[a] [PYR]=0.215 μM; HCOOH 55% w/v; CH_3OH 1% v/v. The errors were calculated by the fitting program.
[b] Ref. [20].

$\phi^{PYR-CB6}/\phi^{PYR}$ is the fluorescence quantum yield ratio between the complexed and the free substrate.

$$F/F_0 = \frac{1 + \left(\phi^{PYR-CB6}/\phi^{PYR}\right) K_A\ [CB6]_0}{1 + K_A\ [CB6]_0} \quad (3)$$

The values for K_A and $\phi^{PYR-CB6}/\phi^{PYR}$ determined at different temperatures from non-linear fitting of the data to Eq. (3) are shown in Table 1 (Fig. 5A). In all cases, the 1:1 relation between PYR and CB6 was confirmed from a linear double reciprocal plot (Fig. 5B) [31]. The K_A values increase proportionally with the temperature.

Despite the differences between substrate concentrations and the substrate/CB6 concentration ratios in absorption and emission spectrocopies, the K_A values are within experimental error, corroborating the 1:1 guest–host stoichiometry of the complex in these acidic media. The comparison of binding constants measured in different media must be treated with caution since in acidic media H^+ competes with the guest [1].

The K_A values are in the some order of those reported in the literature for the complexes of PYR with αCD and βCD ($K_A^{PYR-\alpha CD}=148.4\ M^{-1}$ and $K_A^{PYR-\beta CD}=492.8\ M^{-1}$, respectively [34]). Moreover γCD encapsulates PYR forming a more stable complex ($K_A^{PYR-\gamma CD}=1130\ M^{-1}$ [34]).

The stability of the PYR–CB6 complex is weaker compared to the interaction between this macrocycle and other substrates that show a better match size and electronic complementary, as 1,4-diaminobenzene ($K_A^{1,4-diaminobenzene-CB6}=1860\ M^{-1}$ [35]). Nevertheless, the same behavior of the system studied here was observed with other aromatic compounds, such as substituted benzenes and naphthalenes ($K_A^{benzene-CB6}=27\ M^{-1}$ [36], $K_A^{p-nitroaniline-CB6}=177\ M^{-1}$ [37], $K_A^{\beta-naphthylamine-CB6}=124\ M^{-1}$ [37], $K_A^{2,6-ANS-CB6}=56\ M^{-1}$ [14], $K_A^{phenolblue-CB6}=92.8\ M^{-1}$ [38]).

The ratios $\phi^{PYR-CB6}/\phi^{PYR}$ were higher than five demonstrating a decrease in the non-radiative rate constants suggesting that the complexation with CB6 favors the fluorescent emission by a different microenvironment in relation to the solution and/or to the protected excited fluorophore from the action of inactivating species.

3.3. Thermodynamic parameters

The enthalpy and entropy changes of the studied complexation reaction were obtained from van't Hoff plot (linear plot not shown, correlation coefficient=0.999). The Ln K_A values of the constants determined in HCOOH 55% w/v were plotted against $1/T$. The ΔH and ΔS parameters were calculated from the slope and the intercept of the graph, respectively ($\Delta H=(13\pm1)$ kJ mol^{-1} and $\Delta S=(92\pm3)$ J mol^{-1} K^{-1}). The value of the Gibbs free energy for the system at 298 K indicates an energetically favorable reaction ($\Delta G=-14$ kJ mol^{-1}). These results suggest that entropic factors ($T\Delta S=27$ kJ mol^{-1}) are the dominant driving force for the complex formation between PYR and CB6.

The interaction between neutral guest and CBs has been scarcely explored. Recently, more attention was focused in the interpretation of the driving forces for the complexation between CB and neutral compounds [39,40]. In these cases, the hydrophobic enthalpic factor has been mentioned as the mainly responsible force for the complex formation.

The results obtained in the present study for the PYR:CB6 complex indicate that the hydrophobic entropic force is the main contribution for the complexation. Important entropic effects had previously been observed for some 1,6-diaminohexa-2,4-diyne derivatives [41], amino acids and dipeptides [42], or chiral compounds [43], between others. In these cases, the entropic gain arises from the less disruption to the solvent structure when the complex is formed.

3.4. Characterization of the solid complex

The thermal behaviors of pure PYR, pure CB6, a physical mixture of PYR and CB6 and the solid PYR–CB6 complex were studied in 1:1 molar ratio (Fig. 6). The thermal curve of CB6 displays a broad peak between 30 °C and 230 °C, associated with the release of water molecules encapsulated in the macrocycle [44]. The second endothermic effect with a significant enthalpy (712.6 J g^{-1}) and an important loss of mass corresponds to the main step of decomposition of the macrocyclic compound [44].

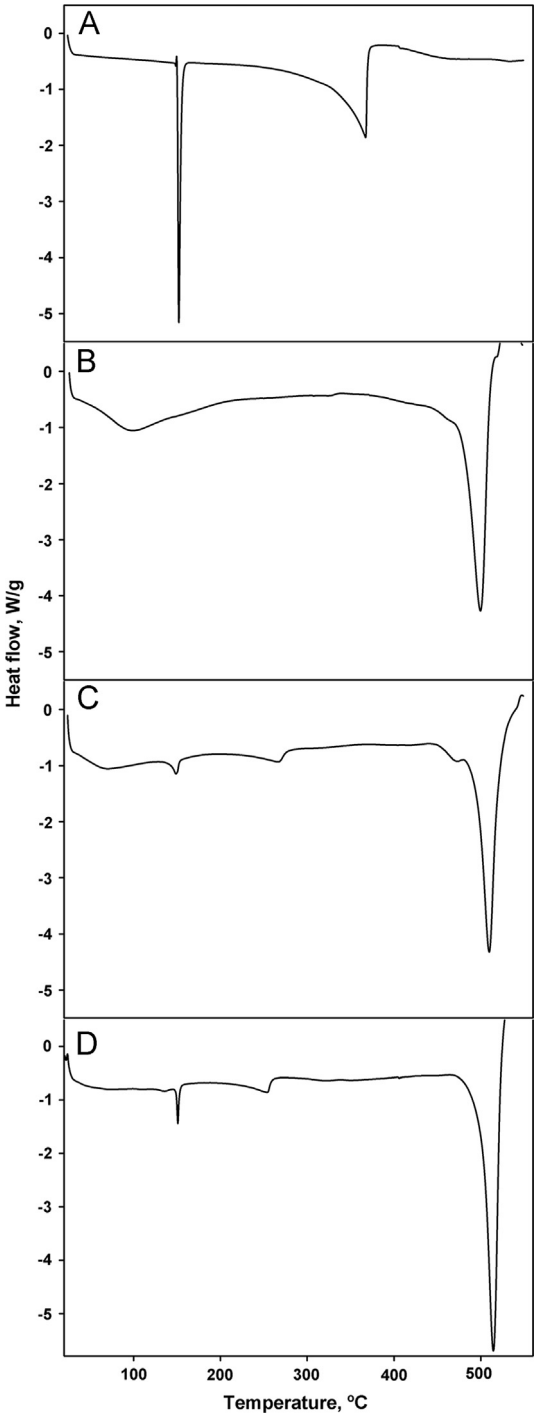

Fig. 6. DSC curves for: (A) PYR; (B) CB6; (C) physical mixture and (D) PYR–CB6 complex.

In the DSC curve of the complex, the broad peak related to the release of water from the CB6 cavity is not observed and the endothermic peak of the CB6 decomposition showed a slight shift. The endothermic peak attributed to the melting of PYR (151.95 °C) showed a slight variation and a remarkable decrease on the intensity in presence of CB6. The DSC scan of the physical mixture differs from the complex curve. Nevertheless, the shift of the endothermic peaks of PYR and CB6 could suggest an interaction established by the simple mixture of both compounds.

Spectroscopic evidences (UV–vis, NMR) suggested complex formation between benzene and CB6 [45], although the structural parameters of CB6 (portal diameter: 3.9 Å; cavity diameter: 5.8 Å; cavity volume: 164 $Å^3$; outer diameter: 14.4 Å; height 9.1 Å) [24] indicate that no interaction is possible with benzene ring which has van der Waals dimensions (6 Å diameter × 4 Å thick) larger than the estimated internal cavity of CB6. The phenomenon was associated with the encapsulation of the aryl ring into the cavity of CB6, which provides a nonpolar environment like a hydrocarbon solvent. In this work was also shown that [45] the cavity of CB6 can accommodate the benzene ring of arylamines with different affinity depending of the substituents of the arene. These antecedents and the results shown here suggest the partial inclusion or a suspended complex of PYR (probably an extreme of one benzene) with the CB6, as it is described for the benzidine-CB6 and tolidine-CB6 complexes [37].

The preceding interpretations of the observed changes in the fluorescence, UV–visible and DSC curves of PYR produced by CB6 were mainly based on the evidence of complex formation, hydrophobic interactions and literature data [45], but these techniques provide limited structural information on the geometry and mode of complexation. Direct evidence in solution could be obtained from NMR studies, which would show some specific interactions between specific parts of the guest and host, and thus direct evidence of a particular mode of interaction. In the case studied here, the insolubility of the minimum concentration of PYR required for a NMR experiment (~1 to 10 mg in 0.5 mL) in the aqueous acidic media necessary for CB6 solubilization (solubility of PYR in water at 25 °C, ~0.1 mg/L) makes impossible these analyses.

4. Conclusions

The complex formation between PYR and CB6 was observed by UV–vis and spectrofluorimetry. In base to the respective spectroscopic changes, the values of K_A were determined by the two techniques with good agreement. The ratio 1:1 PYR:CB6 was confirmed in both cases. Also, the DSC experiments confirm the complex formation. The thermodynamic parameters indicate that the interaction between PYR and CB6 is favored by hydrophobic entropic factors.

Acknowledgments

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