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Thermodynamic approach for studying both the retention and complexation mechanisms with hydroxy-propyl-β-cyclodextrin of a phenoxy-propionic acid herbicide series

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Abstract

The retention and complexation mechanisms of a herbicide series were studied from a chromatographic approach using a novel column called "Nautilus®". The effects of water fraction and the hydroxy-propyl-β-cyclodextrin (HP-β-CD) concentration in the mobile phase were analysed in relation to the column temperature. Two retention models of phenoxy-propionic acid (PPA) derivatives were investigated. It was shown that the retention mechanism was led by free PPA herbicide for low HP-β-CD concentrations and by the PPA/HP-β-CD complex for the highest ones. In addition, an enthalpy–entropy compensation study revealed that both the solute retention and complexation mechanisms were independent of the number of chlorine atoms in the structure. Also the thermodynamic results showed that (1) the retention process depended on the water fraction (*X*) in the mobile phase and (2) the PPA/HP-β-CD complexation mechanism was shown to be entropically controlled.

Keywords: Thermodynamic; Complexation; Retention; Nautilus®; Herbicides

1. Introduction

Phenoxy-propionic acids (PPA) are a chemical class of herbicides (Fig. 1). They are widely used in cereal crops as weed-killers. However, they could present a human toxicity with potential carcinogenic properties and an endocrine dysfunction [1,2]. This molecule series also presents a strong toxicity for the aquatic ecosystem [3]. Indeed, the PPA could show a high risk of persistence by accumulation in the sediments, because of their high hydrophobic character. To eliminate these molecules from soil, it could be possible to increase their hydro-solubility, in particular by the formation of an inclusion complex between PPA and hydroxy-propyl-β-cyclodextrin (HP-β-CD).

Cyclodextrins (CD) are a group of cyclic oligosaccharides made of six, seven or eight (α, β and γ-CD, respectively) monomeric glucopyranose units. The CD contain an hydrophobic cavity enabling encapsulation of a guest molecule and the formation of inclusion complexes [4,5]. The CD usually employed are the β-CD, which can be substituted on hydroxyl groups to increase their aqueous solubility, and also used as chiral selector in some experimental conditions [6–9]. Thus, HP-β-CD, a β-CD derivative, which has a greater stability than the non-substituted β-CD, is tested to form an inclusion complex with hydrophobic molecules as PPA.

Various methods have been described to determine the stoechiometry and the association constants of complexes: UV–visible absorption, NMR spectrometry, potentiometry

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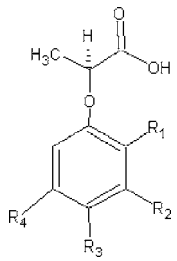

Fig. 1. Phenoxy-propionic acid structures.

[10,11], capillary electrophoresis, calorimetry and fluorescence measurements [5,12,13]. Nevertheless, the RP-HPLC stays the most commonly used procedure [14–17]. Also, to gain further insight into the complexation mechanism, in a bulk solvent containing a high water fraction, a particular stationary phase called "Nautilus®" will be used.

The aim of this work was therefore to analyse (i) the PPA/HP-β-CD complexation mechanism and (ii) the PPA retention process on this particular stationary phase with a high water fraction in the hydro-methanolic mixture used as mobile phase.

2. Material and methods

2.1. Chemicals

HPLC grade methanol was furnished from Prolabo (Paris, France). Water was obtained from an Elgastat water purification system (Odil, Talant, France) fitted with a reverse osmosis cartridge.

The four phenoxy-propionic acids (PPA) (Fig. 1): 2-phenoxy-propionic acid (2PPA), 2-(2-chlorophenoxy)propionic acid (2-2CPPA), 2-(3-chlorophenoxy)propionic acid (2-3CPPA) and 2-(2,4,5-trichlorophenoxy)propionic acid (2-2.4.5TCPPA) were obtained from Sigma–Aldrich (Saint-Quentin, France). Hydroxy-propyl-β-cyclodextrin was obtained from Roquette (Lestrem, France).

2.2. Apparatus

The chromatographic apparatus was equipped with a constant flow pump model LC10-AT, C-R6A Chromatopac integrator (Shimadzu, Touzart et Matignon, Courtaboeuf, Yveline, France), RHEODYNE (Interchim, Montluçon, France) 7125 injection valve fitted with a 20 μl sample loop, and a Lambda-Max LC spectrophotometer Model 481 UV-Visible detector (WATERS, Saint Quentin, France). The temperature was controlled with an Interchim Crococil oven TM No. 701 (Montluçon, France).

2.3. Chromatographic conditions

The mobile–phase flow rate was maintained at 1 ml min^{-1}. The mobile–phase was an hydro-methanolic mixture with a water fraction (X) (v/v) varying from 0.30 to 1.00. Eight water fractions were included in this range (0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0). The HP-β-CD concentrations added in the mobile phase varied from 0 to 17.5 mM (0, 3.5, 7, 10.5, 14 and 17.5). Experiments were repeated three times and carried out at a 280 nm detection wavelength and in a temperature scale from 20 to 35 °C (20, 25, 30 and 35 °C, respectively). A NUCLEOSIL 100-5 C18 NAUTILUS column (Macherey-Nagel, Hoerdt, France), (150 mm × 4.6 mm i.d, 5 μm particle size) was used.

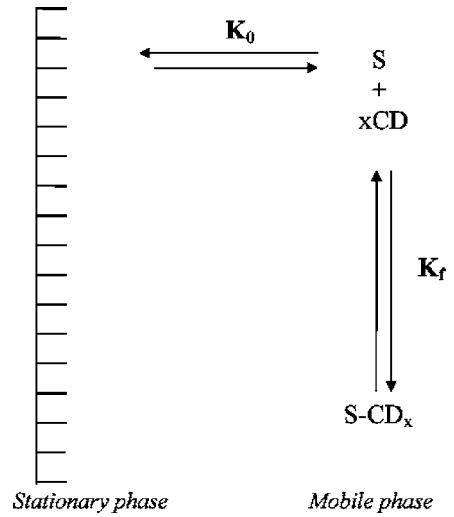

Fig. 2. Chemical equilibria for the model without adsorption of the complex on the stationary phase (first model).

3. Theory

3.1. Model description

Various models have been used to describe the chromatographic retention of a solute when CD is added to the mobile phase [13,14,18,19]. The retention behaviour of a solute in HPLC is based on the partitioning of the solute between the mobile and the stationary phases. Two models are considered in the following section [18,19].

The first model (Eq. (1)) does not take into account the retention of the complex (Fig. 2). Solute retention is split into two independent physicochemical processes, i.e. solute complexation by CD and transfer of free (i.e. uncomplexed) solute from the hydro-methanolic phase to the stationary phase. The solute retention factor (k') is linked to the complex formation constant (K_f) by the following equation [19]:

$$\frac{1}{k'} = \frac{1}{k'_0} + \frac{K_f[CD]^x}{k'_0} \quad (1)$$

where $k'_0 = \phi K_0$ is the solute retention factor without CD in the mobile phase, K_0 is the solute C18 stationary phase association constant without CD, [CD] is the CD concentration in the mobile phase, and x the stoichiometry of the

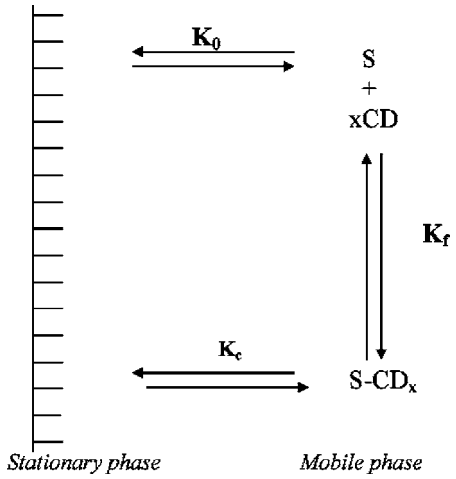

Fig. 3. Chemical equilibria for the model with adsorption of the complex on the stationary phase (second model).

complex. For a 1:1 stoichiometry, a linear plot of $1/k'$ versus [CD] must be obtained and the K_f value can be calculated.

However, it has also been previously demonstrated by Uekama et al. [20] that the complex between the solute and CD may be able to interact strongly with the stationary phase as shown in Fig. 3. This second model (Eq. (2)) takes into account the retention of the complex. k' is linked to the formation constant (K_f) by the following equation:

$$\frac{[CD]^x}{(k_0' - k')} = \frac{1}{(K_f(k_0' - K_c))} + \frac{[CD]^x}{(k_0' - K_c)} \quad (2)$$

where K_c was the complex partitioning coefficient between the stationary and mobile phases. If the complex stoichiometry is 1:1, the plot of [CD] over $(k_0' - k')$ versus [CD] must be linear and the K_f value can be calculated.

3.2. Thermodynamic relationships

The retention behaviour of a solute in HPLC is based on the partitioning of the solute between the mobile and stationary phases. When CD is added to the mobile phase, the solute retention depends on two main physicochemical processes [19]:

- the solute transfer from the hydro-methanolic phase to the stationary phase.
- the complex formation between the CD and the solute in the mobile phase.

The Gibbs free energy (ΔG°) of the solute molecule association either with the C18 stationary phase (retention process) or with the cyclodextrin (complexation process) can be linked to its association constant (δ) according to the well-known equation [13]:

$$\ln(\delta) = \frac{-\Delta G^\circ}{RT} \quad (3)$$

where R is the gas constant and T is the column temperature. As well, ΔG° can be linked to the enthalpic (ΔH°) and entropic (ΔS°) terms of the studied physicochemical process by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

Consequently, the thermodynamic parameters, which allow to determine the retention and complexation mechanisms of solute, are measured as follows:

3.2.1. Thermodynamic retention process

In the transfer mechanism of the solute from the mobile to the stationary phases, the partitioning coefficient ($\delta = K$, retention process) is linked with the retention factor (k') of the solute by the following equation:

$$K = \frac{k'}{\phi} \quad (5)$$

where ϕ was the column phase ratio (volume of the stationary phase divided by the volume of the mobile phase). Combining Eqs. (3)–(5), the relationship between k' and the transfer thermodynamic parameters (ΔH° and ΔS°) is given by the Eqs. (6) and (7):

$$\ln(k') = \frac{-\Delta H^\circ}{RT} + \Delta S^{\circ *} \quad (6)$$

$$\Delta S^{\circ *} = \frac{\Delta S^\circ}{R} + \ln(\phi) \quad (7)$$

where ΔH° and ΔS° are, respectively, the enthalpy and entropy changes accompanying the solute transfer from the mobile phase to the stationary phase.

A plot of $\ln(k')$ against $1/T$ is called a Van't Hoff plot. For linear plot, the slope and intercept are, respectively, $-\Delta H^\circ/R$ and $\Delta S^{\circ *}$. This provides a convenient way of calculating the thermodynamic constants ΔH° and ΔS° if the phase ratio is known or can be calculated. Although ΔS° is not usually provided because of the ambiguity in the phase ratio for commercial columns, $\Delta S^{\circ *}$ varies identically with ΔS°.

These thermodynamic data can be expressed by:

$$\Delta H^\circ = H^\circ_{C18} - H^\circ_{mp} \quad (8)$$

$$\Delta S^\circ = S^\circ_{C18} - S^\circ_{mp} \quad (9)$$

where H°_{C18}, S°_{C18} and H°_{mp}, S°_{mp} are, respectively, the molar enthalpies and entropies of the solute associated with the stationary phase (C18) and with the mobile phase (mp).

3.2.2. Thermodynamic complexation process

In a way similar to the retention mechanism, combining Eqs. (3) and (4), a relationship between the complexation constant ($\delta = K_f$, complexation process), the corresponding thermodymic parameters are independent of the stationary-phase type and are given by:

$$\ln(K_f) = \frac{-\Delta H^\circ_f}{RT} + \frac{\Delta S^\circ_f}{R} \quad (10)$$

In this case ΔH°_f and ΔS°_f are, respectively, the enthalpies and entropies changes accompanying the solute complexation with the CD. The slope and the intercept of this Van't

Hoff plot are, respectively, $-\Delta H^{\circ}_{f}/R$ and $-\Delta S^{\circ}_{f}/R$. This is a convenient way of calculating the thermodynamic constants ΔH°_{f} and ΔS°_{f}.

These thermodynamic data can be also expressed by:

$$\Delta H^{\circ}{}_{f} = H^{\circ\prime}{}_{CD} - H^{\circ\prime}{}_{mp} \quad (11)$$

$$\Delta S^{\circ}{}_{f} = S^{\circ\prime}{}_{CD} - S^{\circ\prime}{}_{mp} \quad (12)$$

where $H^{\circ\prime}{}_{CD}$, $S^{\circ\prime}{}_{CD}$, $H^{\circ\prime}{}_{mp}$ and $S^{\circ\prime}{}_{mp}$ are, respectively, the molar enthalpies and entropies of the solute associated with the cyclodextrin (CD) and with the free solute in the mobile phase (mp).

3.3. Enthalpy–entropy compensation

A further thermodynamic approach to the analysis of a physicochemical process is enthalpy–entropy compensation. This investigation tool has been previously used in chromatographic procedures to analyse and compare the retention or complexation mechanism for a group of compounds [21]. Mathematically, the enthalpy–entropy compensation can be expressed by the following equation [22]:

$$Z^{\circ}_{1} = \beta Z^{\circ}_{2} + Z^{\circ}_{\beta} \quad (13)$$

For the solute retention mechanism, Z°_{1} and Z°_{2} correspond, respectively, to the enthalpy (ΔH°) and entropy (ΔS°) changes during the solute transfer from the mobile to the stationary phases. Z°_{β} is the Gibbs free energy variation (ΔG°_{β}) at the compensation temperature β.

For the complexation process, Z°_{1}, Z°_{2} and Z°_{β} are, respectively, the enthalpy (ΔH°_{f}) and entropy (ΔS°_{f}), and Gibbs free energy ($\Delta G^{\circ}_{f\beta}$) changes accompanying the solute complexation with CD.

According to Eq. (13), when enthalpy–entropy compensation is observed for a group of compounds in a particular chemical transformation, all the compounds have the same Z°_{β} at the compensation temperature β. For example, in liquid chromatography, if enthalpy–entropy compensation is observed, all the solutes of the group will have the same net retention or complexation at the compensation temperature β.

For the solute retention mechanism, combining equations (Eqs. (6) and (13)), the following equation is obtained:

$$\ln(k') = \frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T} - \frac{1}{\beta}\right) - \frac{\Delta G^{\circ}_{\beta}}{R\beta} + \ln(\phi) \quad (14)$$

For the complexation process, combining Eqs. (10) and (13), the following equation is obtained:

$$\ln(K_{f}) = \frac{-\Delta H^{\circ}_{f}}{R}\left(\frac{1}{T} - \frac{1}{\beta}\right) - \frac{\Delta G^{\circ}_{f\beta}}{R\beta} \quad (15)$$

At a constant temperature T, if linear curves ($\ln(k')$ versus $-\Delta H^{\circ}$ and $\ln(K_{f})$ versus $-\Delta H^{\circ}_{f}$) are obtained from Eqs. (14) and (15), the compensation temperature β can be therefore evaluated from the slope. In addition, similar values for the compensation temperature β suggest that the solutes are retained or complexed by identical mechanisms.

4. Results and discussion

4.1. PPA herbicide transfer mechanism from the mobile to the stationary phases without cyclodextrin

The retention factor (k') of each herbicide molecule was measured. All the experiments were repeated three times; the variation coefficients of the k' values were all less than 3%, which indicated high reproductibility and good stability for the chromatographic system. For all the PPA, the retention factors increased with the number of chlorine atoms in their structure. For all the mobile phases used, the elution order of the four PPA was: 2PPA < 2-2CPPA ≈ 2-3CPPA < 2-2.4.5TCPPA. This elution order can be explained by the chlorine atom (electro-attractive), which decreases the electronic density of the benzene ring, leading to an increase of the hydrophobic effect. Moreover, for each water fraction X, linear Van't Hoff plots were obtained with correlation coefficients (r) higher than 0.90 for all fits. The corresponding solute transfer thermodynamic data are given for $X = 0.30$ in Table 1. The negative enthalpies indicated that it was energetically more favourable for the solute to be in the C18 stationary phase. Negative entropies showed an increase in the chromatographic system order when the solute was transferred from the mobile to the C18 stationary phases.

However, an inversion in the retention order has been observed between 2-2CPPA and 2-3CPPA for specific temperatures, at some values of the water fraction (X), called temperature γ. Indeed, the separation of these two compounds depends on their selectivity (α). The difference between the association enthalpy ($\Delta\Delta H^{\circ}$) and entropy ($\Delta\Delta S^{\circ}$) for these species with the C18 stationary phase can be calculated using the following thermodynamic relationship:

$$\ln(\alpha) = -\frac{\Delta\Delta H^{\circ}}{RT} + \frac{\Delta\Delta S^{\circ}}{R} \quad (16)$$

Thus, when α is equal to 1, the two peaks collapse and co-eluted as one peak. One example of $\ln(\alpha) = f(1/T)$ is given in Fig. 4 for a water fraction X equal to 0.7.

Table 1
Values of the transfer enthalpy (ΔH°, kJ mol^{-1}) and entropy ($\Delta S^{\circ *}$) of the PPA solute from the mobile to the C18 stationary phase for $X = 0.30$.

Molecules	ΔH° (kJ mol^{-1})	$\Delta S^{\circ *}$
2PPA	−17.6	−8.5
2-2CPPA	−22.2	−10.1
2-3CPPA	−18.3	−8.5
2-2.4.5TCPPA	−30.7	−13.1

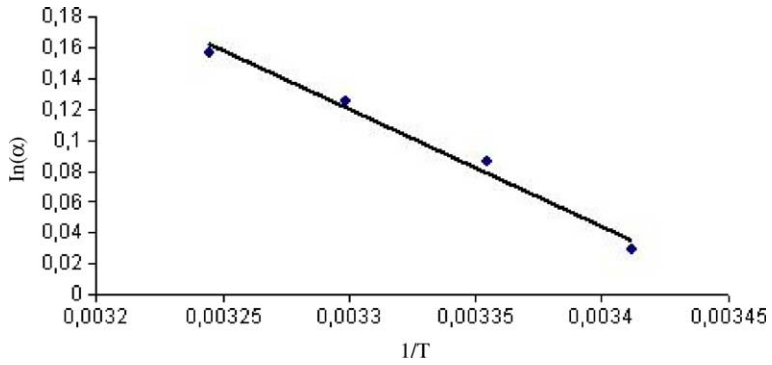

Fig. 4. Plot of ln(α) vs. 1/T for X equal to 0.7.

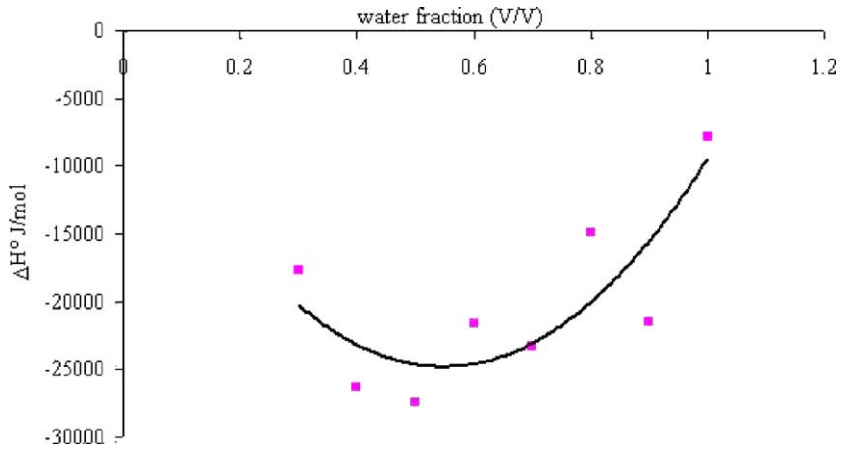

Fig. 5. Plot of ΔH° (J mol^{-1}) vs. X for the 2PPA.

The inversion temperature (γ) is evaluated from:

$$\gamma = \frac{\Delta\Delta H^\circ}{\Delta\Delta S^\circ} \quad (17)$$

These peak inversions (i.e. the change of the elution order between the two adjacent peaks) can be explained by the fact that at these inversion temperatures (Table 2), a perfect equilibrium is obtained between entropic and enthalpic effects governing the recognition mechanism of the C18 stationary phase for 2-2CPPA or 2-3CPPA. Indeed, for a temperature $T > \gamma$, the magnitude of $T\Delta\Delta S^\circ$ is greater than $\Delta\Delta H^\circ$. Thus, the recognition mechanism of C18 for 2-2PPA and 2-3PPA is governed by the difference in their steric constraints in the C18 stationary phase. In this domain, he recognition mechanism was entropically led.

Table 2
$\Delta\Delta H^\circ$ (kJ mol^{-1}), $\Delta\Delta S^\circ$ (J mol^{-1} K^{-1}) and γ ($^\circ K$) values calculated from the selectivity factor (α) between 2-2PPA and 2-3PPA obtained for different water fractions (X)

X	$\Delta\Delta H^\circ$ (kJ mol^{-1})	$\Delta\Delta S^\circ$ (J mol^{-1} K^{-1})	r[a]	γ ($^\circ K$)
0.8	8.1	26.6	0.93	302
0.7	6.5	22.7	0.98	289
0.6	13.9	46.2	0.94	299
0.5	41.8	138.4	0.96	301
0.4	15.2	50.9	0.96	297

[a] r: correlation coefficient of the fit ln(α) versus 1/T.

For a temperature $T < \gamma$, the reverse was observed. The magnitude of $\Delta\Delta H^\circ$ was greater than that of $\Delta\Delta S^\circ$. This was attributed to a favourable contribution of selective interactions (Van der Waals) between 2-2PPA and 2-3PPA with C18. Therefore, in this temperature domain, the recognition mechanism is enthalpically led.

According to Figs. 5 and 6, the enthalpic and entropic data depend on the aqueous fraction in the mobile phase with a critical water fraction ($X_c = 0.50$) for which the solute binding mechanism on the C18 stationary phase changes. It has been known for several years that increasing the water fraction in the bulk solvent, this latter increases its surface tension [13–24]. Therefore, a dual retention process can be described, when the water fraction in the mobile phase increased: (i) the decrease of the herbicide solubility, and (ii) the increase of the surface tension of the bulk solvent. When the water fraction was inferior to X_c, the effect (i) was dominant. Therefore, the solute molar enthalpy and entropy associated with the stationary phase (H°_{C18} and S°_{C18}) decreased and thus ΔH° and ΔS° also decreased (Figs. 5 and 6, Eqs. (8) and (9)). Above X_c, the effect (ii) was dominant and then H°_{mp} and S°_{mp} decreased, leading to an increase of the ΔH° and ΔS° values (Figs. 5 and 6, Eqs. (8) and (9)).

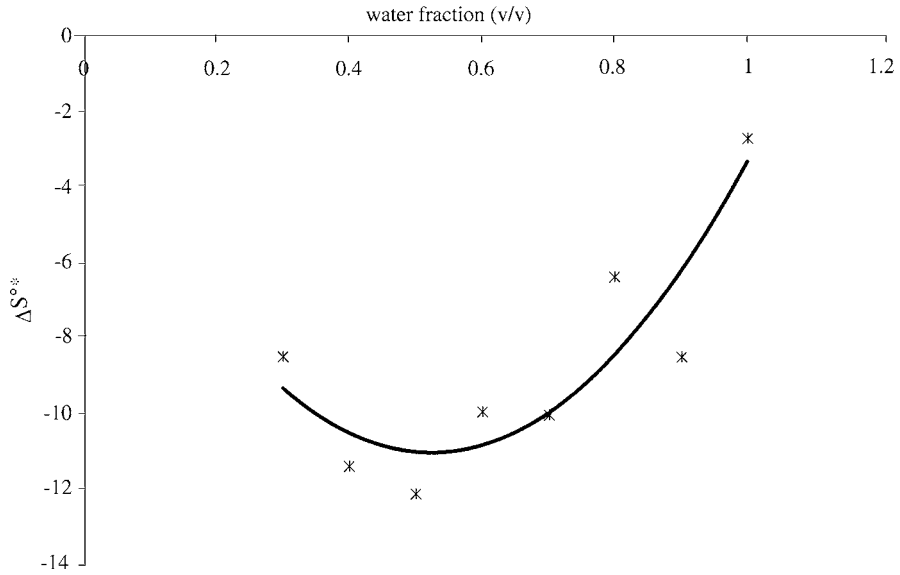

Fig. 6. Plot of $\Delta S^{\circ *}$ vs. X for the 2PPA.

To confirm the retention mechanism change at X_c, plots of $\ln(k')$ versus ΔH° (Eq. (14)) were drawn for the four herbicide molecules. The curves corresponding to two water fractions (X) equal to 0.30 and 1.0 are presented in Fig. 7. The correlation coefficients for the linear fits corresponding to each water fraction in the bulk solvent were always higher than 0.70. These values were in the same range than those previously reported [25,26]and can be considered adequate to verify enthalpy–entropy compensation. This asserts that the interaction mechanism was independent of the herbicide molecular structures, i.e. the number and the position of chlorine atoms. Since the slopes of these linear fits were different (i.e. the compensation temperature β), the binding mechanism of the solute with C18 phase depends on the water fraction of the mobile phase.

4.2. PPA/HP-β-CD complexation mechanism

All the measures were carried out into a mobile phase with a high water fraction (0.80) in order to limit the complexation of methanol with CD and this is the great interest of the Nautilus® stationary phase.

The values of the linear regression coefficients of the two theoretical models were calculated from the Eqs. (1) and (2), respectively. The values obtained from the Eq. (2), which include the transfer of the complex to the stationary phase, are higher than 0.94 and are more discriminating than those obtained from the Eq. (1) ($r < 0.60$). It clearly appears that the behaviour of the PPA is adequately described by the second model (Fig. 3). According to the second model, the complex stoichiometry was determined as 1:1 (HP-β-

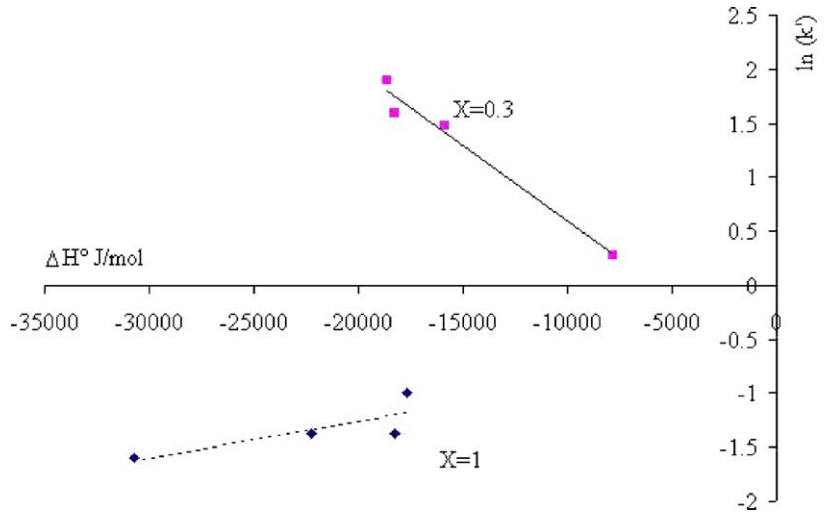

Fig. 7. Enthalpy–entropy compensation represented by plots of $\ln(k')$ against ΔH° ($J\,mol^{-1}$) for $X = 0.3$ and 1.0.

Table 3
K_f values at 30 °C

Molecules	K_f (10^3)
2PPA	0.57
2-2CPPA	1.98
2-3CPPA	1.33
2-2.4.5TCPPA	0.14

Table 4
ΔH_f° (kJ mol^{-1}) and ΔS_f° (J mol^{-1} K^{-1}) values for all the herbicide series

Molecules	ΔH_f° (kJ mol^{-1})	ΔS_f° (J mol^{-1} K^{-1})
2PPA	43.8	23.9
2-2CPPA	52.9	28.7
2-3CPPA	47.2	25.5
2-2.4.5TCPPA	29.3	25.8

CD/PPA) for all the studied PPA. From the different linear fits obtained for each PPA, the K_f values (Table 3) of the different complexes formed were calculated. The K_f values increased in this order: 2-2.4.5TCPPA < 2PPA < 2-2CPPA ≈ 2-3CPPA.

Linear Van't Hoff plots (ln(K_f) versus 1/T) were obtained with a correlation coefficient r higher than 0.86 for all fits. The resulting enthalpy (ΔH_f°) and entropy (ΔS_f°) values for the species complexed with HP-β-CD are positive and are given in Table 4. The positive entropy values can be explained by the fact that the water molecules surrounding PPA were more constrained than those in the bulk solvent (high-energy hydratation shell of water). Indeed, when the complex formation occurs, the PPA are transferred from this well-structured water environment to the less ordered CD cavity. Consequently, the solute complexation process was accompanied by a positive entropy change. The positive enthalpy values were due to the loss of hydrogen bounding between the water molecules when the complexes were formed.

The linear curve of ln(K_f) versus $-\Delta H_f^\circ$ was obtained from equation 15 with a correlation coefficient higher than 0.80; this degree of correlation can be considered to be adequate to verify enthalpy–entropy compensation, thus showing that the complex formation mechanism was independent from the solute molecular structure i.e. the number of chlorine atoms in the molecule.

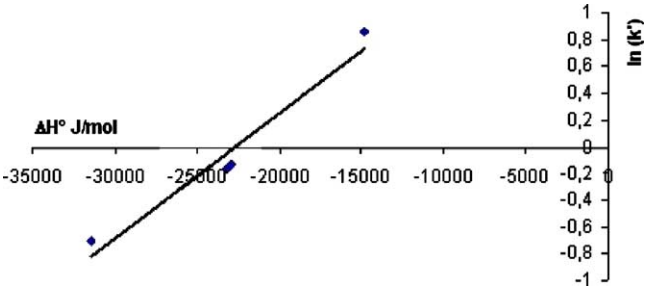

Fig. 8. Plot of ln(k') vs. ΔH° for a concentration of HP-β-CD equal to 10.5 mM.

Table 5
Values of β (°K) for different HP-β-CD concentrations

[CD] (mM)	β °K
0	2785
3.5	1165
7	384
10.5	244
14	249
17.5	199

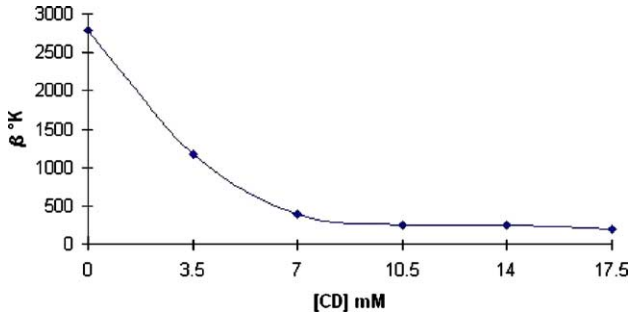

Fig. 9. Plot of β (°K) against HP-β-CD concentration (mM).

The Eq. (14) linearity (ln(k') versus $-\Delta H^\circ$) was examined for all the HP-β-CD concentrations and for all the PPA herbicides and illustrated by an example in Fig. 8 for a [HP-β-CD] equal to 10.5 mM. A linear curve can be drawn for each HP-β-CD concentration. All the obtained straight lines presented a correlation coefficient higher than 0.90 and different slope values, which confirmed that the retention process was independent of the PPA molecular structure. The compensation temperatures β (Table 5) were calculated from the slopes of the previous straight lines. A curve showing the compensation temperature β versus the HP-β-CD concentration (Fig. 9) can be drawn. It then appeared that, for the lowest [HP-β-CD] between 0 and 7 mM, the β values decrease. This observation showed that the retention mechanism was governed by both the free solute and the complex HP-β-CD/PPA transfer from the mobile to the stationary phases (Eq. (2), second model). Thus, in this concentration range, the retention mechanism depends on the [HP-β-CD]. On the contrary, for the highest [HP-β-CD] (>7 mM), the β values were relatively constant, suggesting that all the solute are totally complexed. Then, the retention mechanism was governed by the complex retention and becomes independent from the [HP-β-CD].

5. Conclusion

In summary, two retention models of PPA derivatives were investigated in RPLC with high water fractions and various HP-β-CD concentrations in the mobile phase in relation to column temperature. The obtained results showed that the retention mechanism was controlled by (i) free PPA herbicide retention on C18 stationary phase for low HP-β-

CD concentrations and by (ii) the PPA/HP-β-CD complex retention for the highest ones. As well thermodynamic results demonstrated that the solute retention mechanism was independent of the number of chlorine atoms in the structure, but depended on the water fraction (X) in the mobile phase. The PPA/HP-β-CD complexation mechanism was shown to be the same for all solutes and entropically controlled.

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