Review

Humic Acids Aggregates as Microheterogeneous Reaction Media: Alkaline Hydrolysis Reactions

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Abstract: The influence of humic aggregates in a water solution upon the chemical stability under basic conditions of different substrates was reviewed. The kinetic behavior of each substrate was modeled in terms of a micellar pseudophase model.

**Keywords:** humic acids; alkaline hydrolysis; pseudophase model; micelles

1. Introduction

It is well known that colloidal aggregates constitute true chemical nano-reactors in their different forms. By concentrating the reactants in restricted areas or separating them between the different domains of the system, these reaction media can cause both critical catalytic phenomena and dramatic inhibitions of chemical processes [1–3].

One such reaction medium is micellar aggregates. It is well known the influence of aqueous micelles upon the chemical equilibria and the rate of chemical reactions. Evidences of these effects have been summarized in the literature [4–6]. Micellar catalysis on organic and inorganic reactions has been extensively studied, and it is well known that it is related to the ability of micelles to absorb all types of molecules [7–9]. The reagents incorporation into the micelle is driven by hydrophilic/hydrophobic interactions and electrostatic interactions between the micellar surface and the reagents. In this way, the interaction between the reagents and the micellar aggregate can be modeled by applying the pseudophase model [10]. In this model, bulk water can be considered like one continuous phase and micellar aggregate as another. The reagents would be distributed between both phases, or they would be left behind from one of them. In the same way, the chemical reaction could also occur in both phases or in one of them.

We have introduced the kinetic behavior in the presence of micelles because humic acids have behavior in the aqueous solutions similar to micellar aggregates [11,12].

Humic substances (HSs) represent a significant part of the organic matter that is found in soils and in natural environments. These have a high specific surface area [13–15], with a negative surface charge due to numerous deprotonable carboxylic and phenolic groups (see Scheme 1) [16]. Furthermore, due to amino groups that can be protonated, it enables a positive surface charge. That is why the surface charge has a significant dependence on pH. Full ionized charge capacity (CEC) is 0.3–0.6 mol·kg^{-1}.
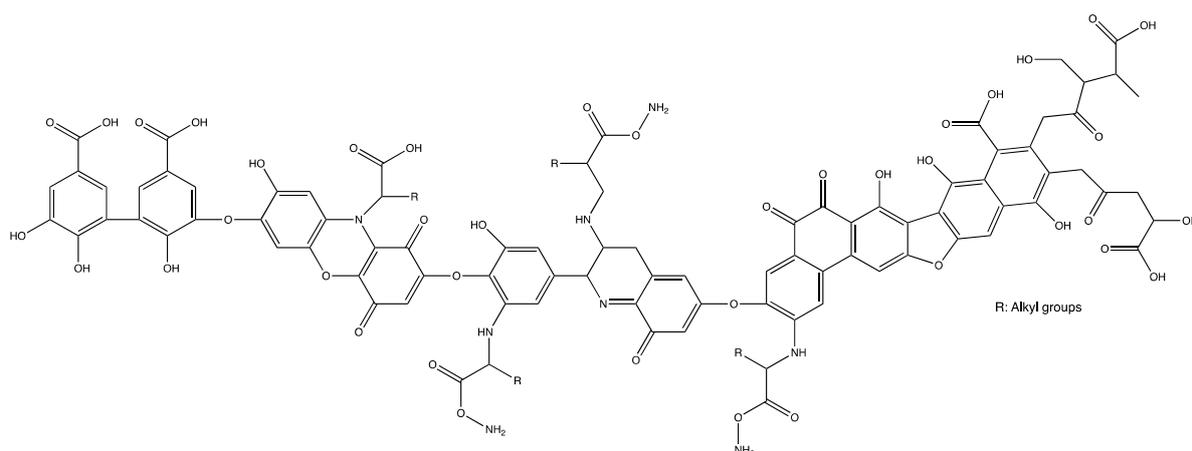
Scheme 1. Model of the humic acid chemical structure.

The basic hydrolysis reaction kinetics of the reagents assessed in this review paper were followed by the first-order conditions ([V] « [OH⁻]), using for this aim Varian Cary 50 Bio spectrophotometer with the thermostated reader cell at (25.0 ± 0.1) °C. The HSs used for these experiments absorb in the UV-vis region, so the spectra were carried out from 200 to 800 nm, using as blank the spectrum of HSs without reaction (in absence of the reagent to study). As previously reported, the disappearance of the shoulder at maximum wavelength was critical to assess the basic hydrolysis of the molecules tested (e.g., $\lambda_{max(VI)}$ = 242 nm, $\lambda_{max(HCF)}$ = 275 nm). The data were recorded in triplicate to ensure the reproducibility of the method. As abovementioned, the data were treated by assuming the conditions of the pseudo-first order and the rate equation to determine the reagents R disappearance as follows:

$$-\frac{\mathrm{d}[R]}{\mathrm{d}t} = k_{\mathrm{w}}[\mathrm{Rs}]_t[\mathrm{OH}^-]_t = k_{\mathrm{obs}}[\mathrm{Rs}]_t \tag{1}$$

where [R] is the reagents concentration, k_{w} is the bimolecular rate, and k_{obs} is the pseudo-first rate constants for the basic hydrolysis of the reagents.

In aqueous solution [17–21], in which HSs acts as micellar-like aggregates, they can adsorb different substrates [22–29] that can act as environmental pollutants [30], increasing or reducing their bioavailability, which is the case of different xenobiotics [31,32] that are persistent in the aquatic environment or soils [33,34]. The role of humates and humic acids in different organic substrates' mobility was conveniently illustrated by Ramus et al. [35,36] and Chiou et al. [37]. Thus, it was shown that when the content of humic substances in solution increases, significant decreases are observed in the mass transfer values at the gas–liquid interface. Furthermore, they can modify pollutants' destination in the environment and act as catalysts in the chemical breakdown of some pollutants [31,38–44]. Previous studies show the effect of HSs in solution on hydrolysis reactions (the main transformation pathway for many xenobiotics in the environment [39,45]. These substrates are typically composed of a marked hydrophobic character that shows a high affinity for HSs aggregates [38–46].

Humic substances are also able to "kidnap" heavy metals [47–54] and interact with minerals [28,49,55,56], modifying the absorption and toxicity of these compounds. There are few studies in the literature in which the catalytic activity of HSs has been compared [25,38,45,46,57,58]. These studies can be critical, considering their possibility in the biogeochemical cycle of elements and the high concentrations of HSs in some natural environments.

In this paper, we will review some of the contributions of our research group [59–63], which has tried to shed light on the role of humic acids and humates in aqueous solution,

as colloidal aggregates, in the catalysis of different basic hydrolysis processes. HSs used in these studies were isolated from soil using the method previously described [64].

2. Hydrolysis of Carbocations

The first group of reactions that we decided to analyze in humic substances was the alkaline fading of stable triaryl methyl carbocations (Scheme 2) [61]. This is because it is a reaction that has already been studied, and these carbocations entangled with different nucleophiles were used to construct of the nucleophilic scale of the Ritchie N^+ family [65,66], which was considered as a challenge to the reactivity–selectivity principle [67,68]. These reasons made it an instrument for studying reactivity in other microorganized environments. One of the first published studies on catalysis was carried out precisely with the basic hydrolysis of crystal violet [69,70]. Subsequently, they were widely used in studies on the catalytic or inhibitory effects of normal micelles [71], reverse micelles or microemulsions [72–74], and other microheterogeneous systems [75]. In this way, we understood that it could be an excellent chemical probe to obtain valuable information on the role of the different factors that affect the general reactivity in HSs micelles, such as the reagents' compartmentalization and the characteristics of the HSs aggregates as reaction medium.

Malachite Green: R: H–
Crystal Violet: R: $(CH_3)_2N–$
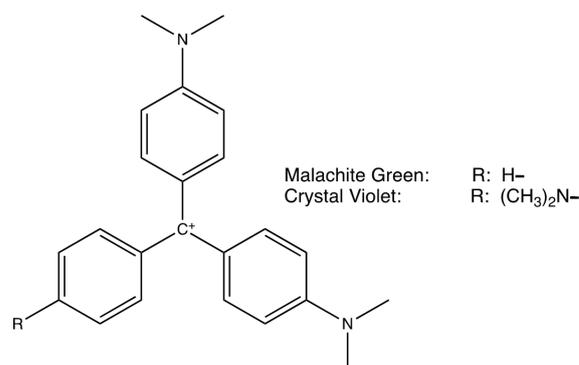
Scheme 2. Crystal violet (CV) and malachite green (MG).

Thereby, the basic hydrolysis of CV and MG in the presence of different concentrations of HSs has been studied under conditions in which all the humic acids are in the form of humate. The presence of HSs has been observed to inhibit the hydrolysis reaction, as shown in Table 1. An inhibition of 4.5 times was observed for the hydrolysis of CV and 24 times for the case of MG.

Table 1. Kinetic parameters of basic hydrolysis of carbocations in the presence of HSs aggregates obtained from the pseudophase model (Equation (2)).

Substrate	$k_w/M^{-1} \cdot min^{-1}$	$K_s/mg^{-1} \cdot L$
CV [61]	1.23 ± 0.02	0.13 ± 0.01
MG [61]	181 ± 6	0.65 ± 0.05

This behavior is justified based on the distribution of the reagents and the different reaction loci in the microheterogeneous system. Thus, the reaction can occur inside the aggregate, on the aggregate's surface (in the Stern layer), or in the bulk solvent. The interior of the aggregate will have a hydrophobic nature. However, the CV or MG housed there could not be exposed to OH^- and therefore would not participate in the reaction. The same would happen on the aggregate's surface since the OH^- would also be excluded due to electrostatic repulsions between the OH^- and the negatively charged groups located on the surface of the aggregate [76,77]. Thus, they only take place in the bulk water, where the OH^- and a part of the carbocations non-associated with the aggregate will be found. Scheme 3 shows the mechanism that takes place in this microheterogeneous system.
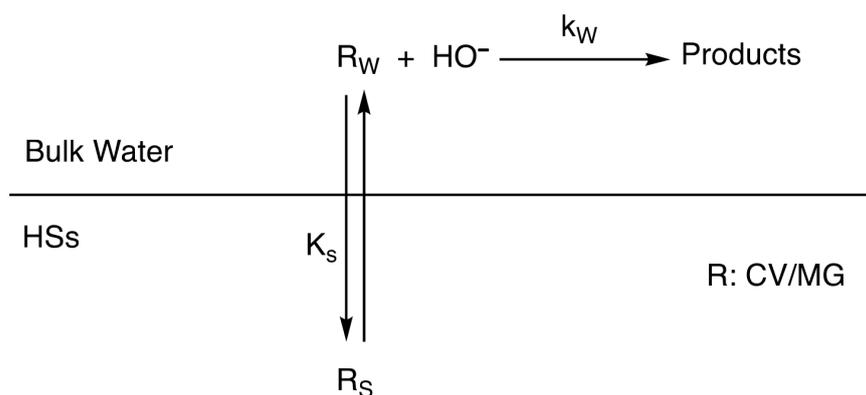
Scheme 3. Pseudophase model for basic hydrolysis of CV/MG in the presence of HSs.

The observed results [61] would be equivalent to those observed in anionic micelles [78]. The observed kinetic behavior complies with the kinetic equation obtained from Scheme 3 (Equation (2)), where the subscripts s and w denote the pseudophase micellar and the bulk water, respectively, and K_s (Equation (3)) is the carbocation association constant to the micellar aggregate, and k_2 is the rate constant in pure water.

$$k_2 = \frac{k_w}{1 + K_s[\text{HSs}]} \tag{2}$$

$$K_s = \frac{[R]_s}{[R]_w[\text{HSs}]} \tag{3}$$

$$\frac{1}{k_2} = \frac{1}{k_w} + \frac{K_s}{K_w}[\text{HSs}] \tag{4}$$

From these equations, we obtained values of the substrate association constants to HSs aggregate. The values obtained were $K_s = (0.13 \pm 0.01)\ \text{mg}^{-1}\cdot\text{L}$ and $K_s = (0.65 \pm 0.05)\ \text{mg}^{-1}\cdot\text{L}$, respectively, for the CV and the MG. This higher value of K_s observed for the MG versus the CV is due to the lower polarity of the first versus the second, with which it would be expected that it would penetrate more deeply into the HSs [60]. Figure 1 shows the fit of experimental results to linearized Equation (2) (Equation (4)). Table 1 shows the kinetic parameter for these reactions.
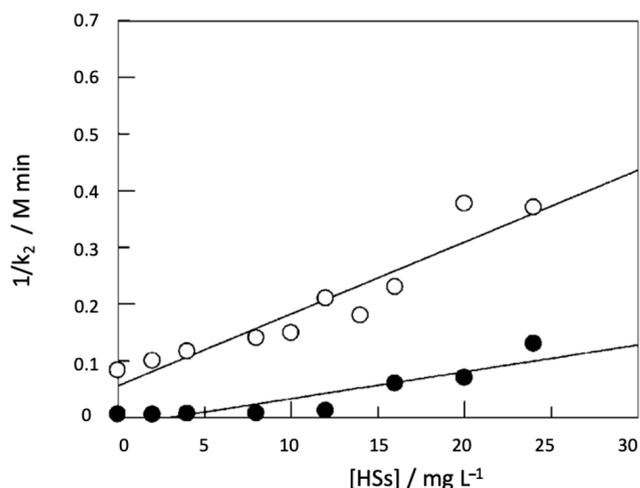

Figure 1. Pseudophase model (Equation (4)) fit of experimental results for basic hydrolysis of CV (○) and MG (●) in the presence of humic aggregates. $T = 25\ °C$.

3. Hydrolysis of N-Methyl-N-nitroso-p-toluene Sulfonamide

Another molecule of interest whose study was approached in our laboratory was N-methyl-N-nitroso-p-toluenesulfonamide (MNTS) [54] (see Scheme 4), which is of biological interest [79] because it is well known that nitrosulfonamides are very effective nitrosating agents [68]. Another advantage of this molecule is the detailed research of our team of the mechanisms of its hydrolysis reactions (both acidic and basic) together with the mechanisms of the transnitrosation processes that involve it, both in homogeneous and microheterogeneous media [1–3,5,80–83]. That is why we consider it as a suitable chemical probe for its study in aggregated HSs since it could be a valuable tool for deepening the knowledge of the chemical reactivity in the presence of HSs micelles, complementing the previous observations acquired from the study of the processes of hydrolysis of CV and MG (vide supra).
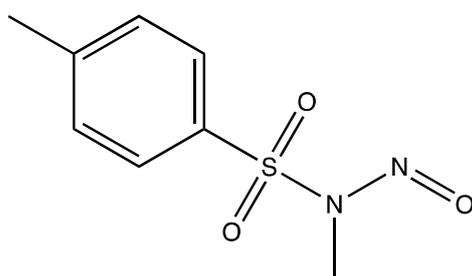
Scheme 4. N-methyl-N-nitroso-p-toluenesulfonamide (MNTS).

As in the previous section, the presence of aggregated HSs inhibits the basic hydrolysis of MNTS by the association of MNTS with the aggregates. Again, this behavior was modeled using the pseudophase model. Considerations like those applied for CV, and MG, led us to propose a mechanism like that of the previous ionic compounds, such as the one shown in Scheme 3, so that, once again, the corresponding kinetic equation would be Equation (2) and the distribution of the MNTS would be governed by Equation (3). From the adjustment of the experimental results to Equation (2), a value for $K_s = (25 \pm 2)$ mg^{-1}·L was obtained (see Figure 2).
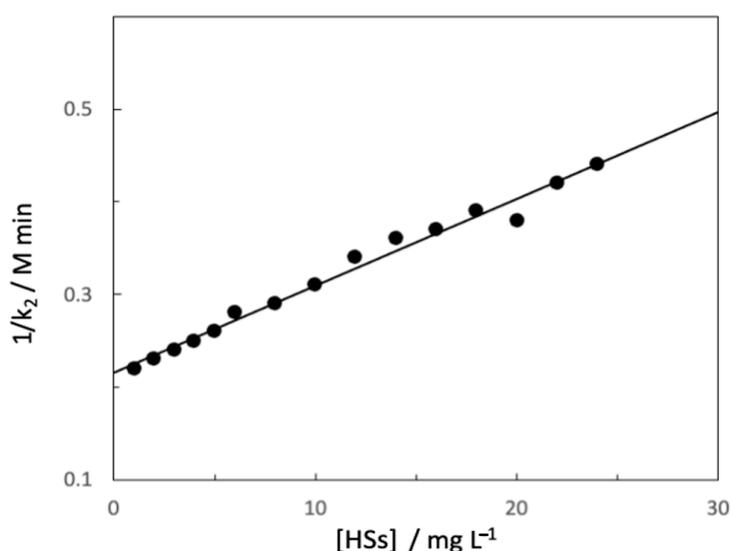

Figure 2. Pseudophase model (Equation (4)) fit of experimental results for basic hydrolysis of MNTS in the presence of humic aggregates. $T = 25\ ^\circ$C.

4. Hydrolysis of Carbofuran and Derivatives, Iprodione, and Vinclozolin

Previous results show that the comparability presented by the HSs aggregates have a kinetic behavior analogous to the conventional micellar aggregates. With the study of the basic hydrolysis of both ionic substances (MG and CV) [60] and with non-ionic substances (MNTS [54]), the validity of the micellar pseudophase model was demonstrated beyond any doubt. For this reason, the stability of different xenobiotics in basic media and in the presence of HSs in aqueous solution was discussed below. In this way, the basic hydrolysis of carbofuran (CF) [62] and two derivatives of carbofuran [62]—3-hydroxy-carbofuran (HCF) and 3-keto-carbofuran (KCF), as well as iprodione (IP) [61] and vinclozolin (VI) [59] in the presence of HSs, were analyzed, and their behavior was compared with similar results in ionic and non-ionic micelles. Scheme 5 shows the xenobiotics under study.


Carbofuran (CF)   3-Hydroxy-Carbofuran (HCF)   3-KetoCarbofuran (KCF)

Iprodione (IP)   Vinclozolin (VI)
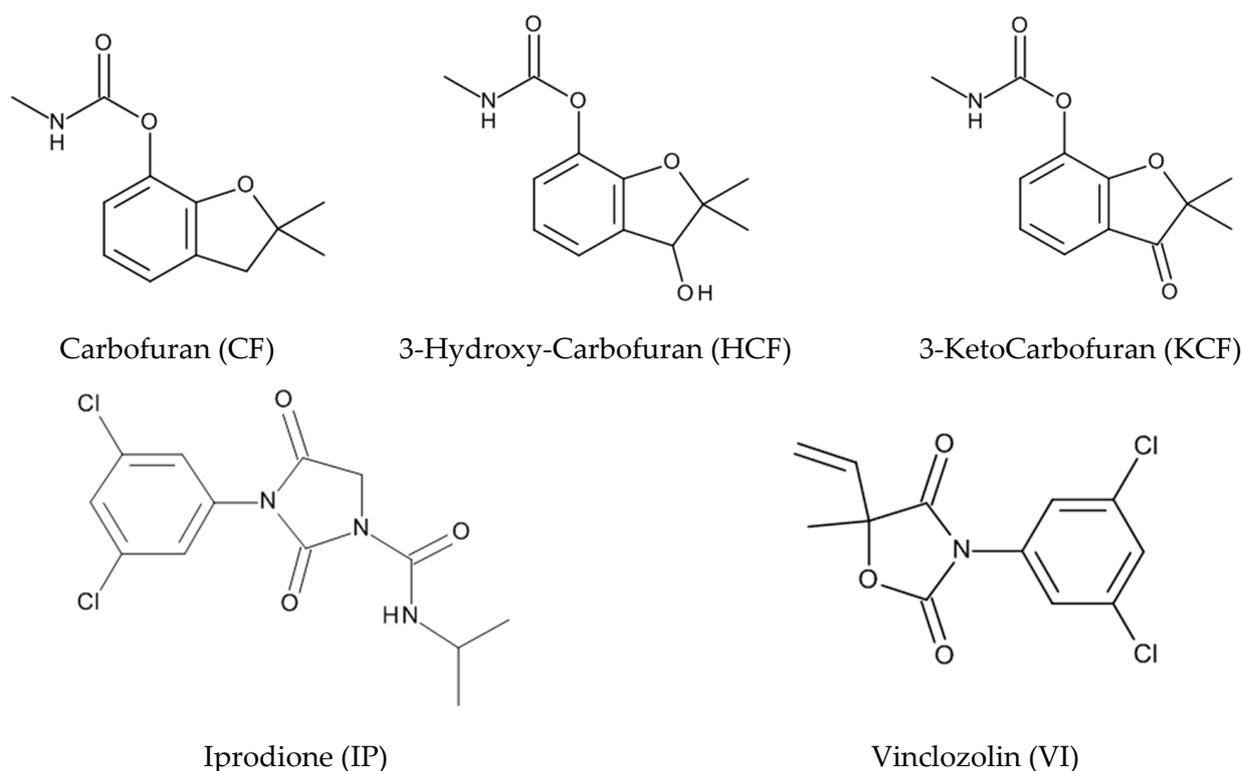
Scheme 5. Carbofuran and carbofuran derivatives, iprodione (IP), and vinclozolin (VI).

In the case of carbamates, a curious behavior was observed since we found an inhibition on the basic hydrolysis of HCF [62] and KCF [62], justifiable, as in the previous cases, based on the association of the substrates to the aggregate and the exclusion of OH$^-$ from their vicinity based on electrostatic considerations (vide supra). When the experimental data is fitted to a mechanism similar to that used for the case of MNTS and ionic compounds, (Scheme 3) (Equations (2) and (3)) we obtain values of the constant in water of $k_w = (1.86 \pm 0.06) \times 10^2$ M^{-1}·min^{-1} and $k_w = (11.4 \pm 0.6) \times 10^3$ M^{-1}·min^{-1} and some values of association constants of $K_s = (1.0 \pm 0.1) \times 10^{-2}$ mg^{-1}·L and $K_s = (5 \pm 1) \times 10^{-3}$ mg^{-1}·L, respectively, for HCF and KCF. However, no effect is found on the reaction rate for CF [62] hydrolysis, so we must assume that in this case, CF absorption does not occur inside the HSs aggregate, and all the CF remains in the bulk water. Table 2 shows the kinetic results obtained and Figure 3, as an example, shows the pseudophase model fit of experimental results for basic hydrolysis of carbofuran and carbofuran-derivatives.

Table 2. Kinetic parameters of basic hydrolysis different xenobiotics in the presence of HSs aggregates obtained from the pseudophase model (Equation (2)).

Substrate	$k_w/M^{-1}\cdot min^{-1}$	$K_s/mg^{-1}\cdot L$
CF [62]	$(0.66 \pm 0.06) \times 10^2$	0
HCF [62]	$(1.86 \pm 0.06) \times 10^2$	$(1.0 \pm 0.1) \times 10^{-2}$
KCF [62]	$(11.40 \pm 0.60) \times 10^3$	$(5.0 \pm 1.0) \times 10^{-3}$
IP [61]	$(1.88 \pm 0.01) \times 10^3$	$(1.4 \pm 0.1) \times 10^{-2}$
VI [59]	$(8.20 \pm 0.40) \times 10^2$	$(9.7 \pm 0.1) \times 10^{-2}$
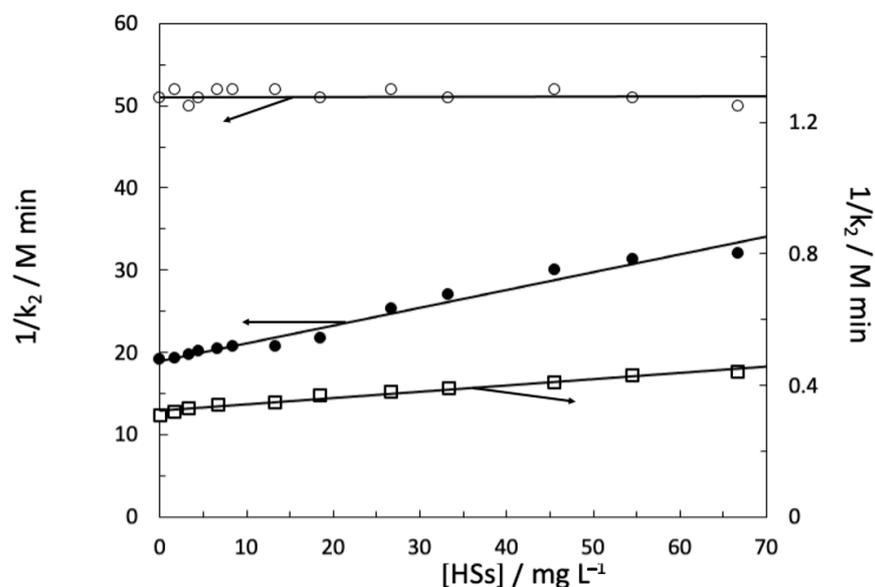
Figure 3. Pseudophase model (Equation (4)) fit of experimental results for basic hydrolysis of CF (○), HCF (●), and KCF (□) in the presence of humic aggregates. T = 25 °C.

When the basic hydrolysis of iprodione (IP) [61] was analyzed, inhibition was also observed. This behavior indicates that the mechanistic model applied in the case of carbofuran and carbofuran-derivatives is still valid. In this case, a slightly higher inhibition was observed than in the previous cases. In the case of carbofuran-derivatives, an inhibition of ~1.7- and 1.5-fold, respectively, had been found for the case of HCF and KCF (we must remember that we had not found an effect of the presence of HSs aggregates on the basic hydrolysis of CF) while in the case of the IP, the decrease in speed was 2-fold.

As in the previous cases, from Equation (2), we have obtained the corresponding kinetic parameters. A rate constant for the hydrolysis process in bulk water of $k_w = (1.878 \pm 0.006) \times 10^3$ M^{-1}·min^{-1} and an association constant to the addition of $K_s = (1.40 \pm 0.10) \times 10^{-2}$ mg^{-1}·L (Table 2). The higher value of the observed K_s would justify the greater inhibition observed on the hydrolysis of the IP compared to the carbofuran-derivatives.

Regarding the results obtained for the basic hydrolysis of vinclozolin (VI) [59], the inhibition observed due to the presence of HSs aggregates was much more dramatic, obtaining a decrease in the reaction rate of 9-fold. When the basic hydrolysis of iprodione (IP) was analyzed, inhibition was also observed. By applying the pseudophase model and adjusting the experimental data to Equation (2), we obtain an association constant to the aggregate significantly higher than in the previous cases, $K_s = (9.7 \pm 0.1) \times 10^{-2}$ mg^{-1}·L (Table 2). The greater affinity of the VI towards the HSs aggregates would cause this more significant inhibition observed on the basic hydrolysis in this compound.

5. Binding Constants and Hydrophobicity of HSs Core

Because of the units of K_s, it is not possible to apply a direct comparison of this value with the corresponding ones for normal micelles to evaluate the HSs core's hydrophobicity.

However, with the data obtained for the different hydrolysis reactions discussed in the previous sections, we can compare the ratios between the association constants obtained for aggregated HSs and normal micelles.

In the literature, there are abundant studies that obtain the association constants of some of these compounds (MNTS [82,84–86] and CV [75,87]) to a large number of micelle aggregates, finding a linear correlation between $K_s(MNTS)/K_s(CV)$ and the length of the hydrocarbon chain of traditional surfactants. Thus, the $K_s(MNTS)/K_s(CV)$ ratio in the presence of HSs aggregates is 192. For the OTACl (octadecyl trimethyl ammoniumchloride), we find that $K_s(MNTS)/K_s(CV)$ has a value of 10, that is, 19 times less than that found for HSs. In the case of SDS (sodium dodecyl sulfate), the value of $K_s(MNTS)/K_s(CV)$ would have a value of 4.3, in this case, 45 times less than the corresponding one for HSs. Figure 4 shows the ratio value between MNTS and CV binding constants to different chain length surfactants. It is, therefore, evident that the core of aggregate HSs is drastically more hydrophobic than that of traditional micelles, both anionic and cationic.
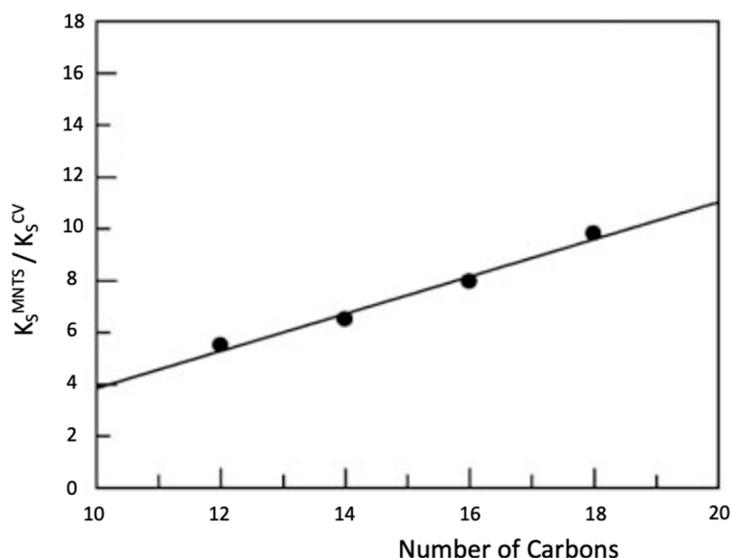

Figure 4. Binding constants ratio between MNTS and CV to normal micelles as a function of the chain length of surfactants. $T = 25\,^\circ\text{C}$.

Furthermore, it is evident that the hydrophilic/hydrophobic interactions are the main driving force behind the association of the different substrates to the aggregate, as evidenced by the evident correlation between the log$P$ values of the substrates and the association constants found from the adjustment of the experimental data to the micellar pseudophase model (see Figure 5).
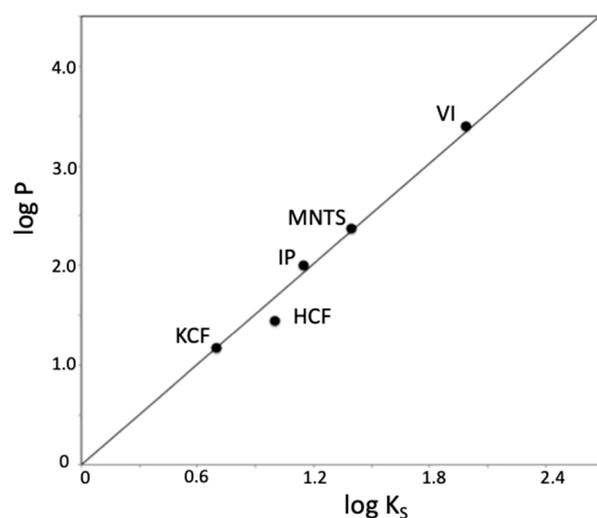
Figure 5. Relationship between $\log K_s$ for different substrates (KCF, HCF, IP, MNTS, VI) in humic aggregates and the $\log P$ value for each substrate. $T = 25$ °C.

6. Conclusions

In summary, the effect of the presence of micelles formed by HSs on the basic hydrolysis reactions results in an inhibition due to the exclusion of OH^- from the Stern layer of the aggregate due to the electrostatic interactions between the negative surface charge of the HSs and the OH^- ion. In this way, the inhibitions would be due to the inclusion of the different substrates inside micelles, protecting them from a nucleophilic attack by OH^-.

The hydrophilic/hydrophobic interactions are the main driving force behind the association of the different substrates to the aggregate, which has been demonstrated due to the evident correlation between the $\log P$ values of the different substrates and their binding constants.

Therefore, when comparing the constants obtained in the presence of HSs with the constants of association to other micellar aggregates, it can be concluded that the core of the aggregates of HSs has a hydrophobic character significantly greater than that of "usual" micelles of sodium alkyl sulfate, alkyl trimethyl ammonium chloride or alkyl pyridinium chloride, even for hydrocarbon chains of more than 18 carbon atoms.

Abbreviations

CEC	ionized charge capacity
CF	carbofuran
CV	crystal violet
HCF	3-hydroxy-carbofuran
HSs	humic substances
IP	iprodione
KCF	3-keto-carbofuran
MG	malachite green
MNTS	N-methyl-N-nitroso-p-toluenesulfonamide
OTACl	octadecyl trimethyl ammonium chloride
SDS	sodium dodecyl sulfate
VI	vinclozolin

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