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Review

Humic acids aggregates as microheterogeneus reaction media: Alkaline hydrolysis reactions

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

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

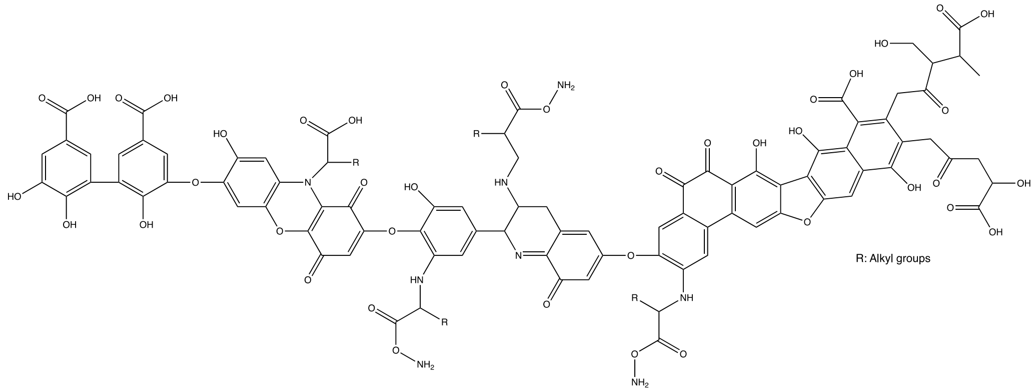
1. Introduction

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

One such reaction medium is micellar aggregates. In fact, it has long been known that aqueous micelles significantly influence both the equilibrium and the rate of chemical reactions, as evidenced by the extensive literature on this topic[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 incorporation of the reagents into the micelle is driven by both 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 as one phase and micellar aggregate as other. In this case, 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 take place in both phases or in one of them.

We have introduced the kinetic behavior in the presence of micelles because humic acids have a behavior in aqueous solution like micellar aggregates[11,12].

Humic substances (HSs) represent a significant part of the organic matter that we can find in soils and in natural environments. These have a high specific surface area[13,14], with a negative surface charge due to the presence of numerous deprotonable carboxylic and phenolic groups. Furthermore, due to the presence of amino groups that can be protonated, it enables the presence of a positive surface charge. That is why the surface charge has a large dependence on pH. Full ionized charge capacity (CEC) is 0.3-0.6 $\mathrm{mol}_{(+)}\mathrm{kg}^{-1}$.



Scheme 1: Model of Humic Acid chemical structure[15]

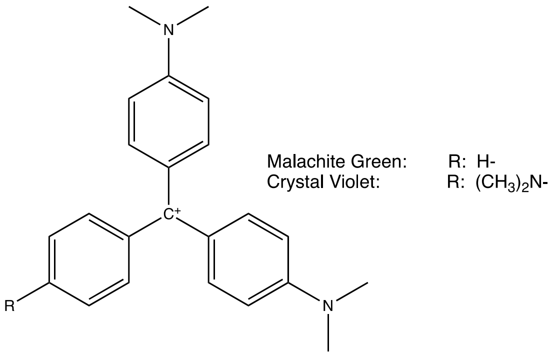
In aqueous solution[16–19], in which HS acts as micellar-like aggregates, they can adsorb different substrates[20–26] that can act as environmental pollutants increasing or reducing their bioavailability. This is the case of different xenobiotics[27,28] that can be persistent in the aquatic environment or in soils[29,30]. The role of humates and humic acids in different organic substrates mobility was conveniently illustrated by Ramus et al.[31,32] 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, also, act as catalysts in the chemical breakdown of some pollutants[27,33,34]. Previous studies show the effect of HS in solution on hydrolysis reactions (the main transformation pathway for many xenobiotics in the environment[34,35]. These substrates are normally composed of a marked hydrophobic character that show a high affinity for HS aggregates[33–36].

Humic substances are also able to "kidnap" heavy metals[37–44] and interact with minerals [45–47], modifying the absorption and toxicity of these compounds. There are few studies in the literature in which the catalytic activity of HS has been compared[23,33–36,48,49]. These studies can be very important, considering their possible in the biogeochemical cycle of elements and the high concentrations of HS in some natural environments.

In this paper we will review some of the contributions of our research group[50–54] that 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.

2. Hydrolysis of carbocations[51]

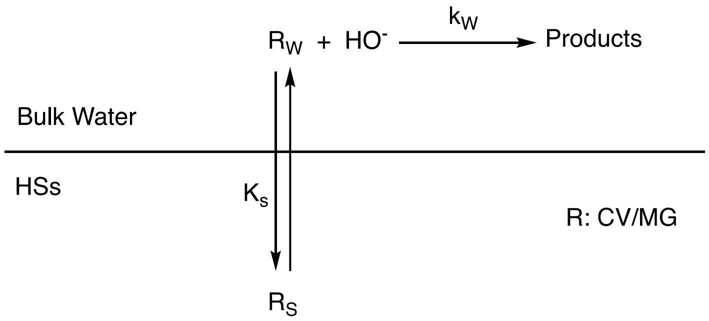
The first group of reactions that we decided to analyze in the presence of humic substances was the alkaline fading of stable triaryl methyl carbocations (Scheme 2). This is because it is a reaction that has alredy been studied and that these carbocations entangled with different nucleophiles was used for the construction of the nucleophilia scale of the Ritchie N^+ family[55,56] which it was considered as a challenge to reactivity-selectivity principle[57,58]. These reasons made it an instrument for studying reactivity in other microorganized environments. In fact, one of the first published studies on honeydew catalysis dealt precisely with the basic hydrolysis of crystal violet[59,60]. Subsequently, they were widely used in studies on the catalytic or inhibitory effects of normal micelles[61], reverse micelles or microemulsions[62–64] and other microhetoerogeneus systems[65]. 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 HS micelles, such as the compartmentalization of the reagents and the characteristics of the HS aggregates as reaction medium.



Scheme 2: Crystal Violet (CV) and Malachite Green (MG)

In this way, the basic hydrolysis of CV and MG in the presence of different amounts of HSs has been studied under conditions in which all of the humic acid is 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.

This behavior is justified based on the distribution of the reagents and the different reaction loci in the microeterogeneous system. Thus, the reaction can take place inside the aggregate, on the surface of the aggregate (in the Stern layer) or in the bulk solvent. It is evident that the interior of the aggregate will have a hydrophobic nature, however, the CV or MG that are housed there could not be exposed to HO- and therefore would not participate in the reaction. The same would happen on the surface of the aggregate, since the HO- would also be excluded due to electrostatic repulsions between the HO- and the negatively charged groups located on the surface of the aggregate[66,67]. In this way, the only take place in the bulk water, where the HO- 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 presence of HSs

The observed results[51] would be equivalent to those observed in anionic micelles[68]. The observed kinetic behavior complies with the kinetic equation obtained from Scheme 3 (eq 1), were the subscripts *s* and *w* denote the pseudophase micellar and the bulk water respectively and K_s (eq 2.) is the carbocation association constant to the micellar aggregate.

$$k_2 = \frac{k_W}{1+K_s[HSs]} \qquad [1]$$

$$K_s = \frac{[R]_s}{[R]_W[HSs]} \qquad [2]$$

$$\frac{1}{k_2} = \frac{1}{k_w} + \frac{K_s}{k_w}[HSs] \qquad [3]$$

From this equation, we were able to obtain values of the substrate association constants to HSS aggregate. The vales obtained were K_s = (0.13±001) mg^{-1}L and K_s = (0.65±0.05) mg^{-1}L respectively for the CV and the MG. This higher value of K_s observed for the VM 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[51]. Figure 1 shows the fit of experimental results to linearized eq 1 (eq 3). Table 1 shows the kinetic parameter for these reactions.

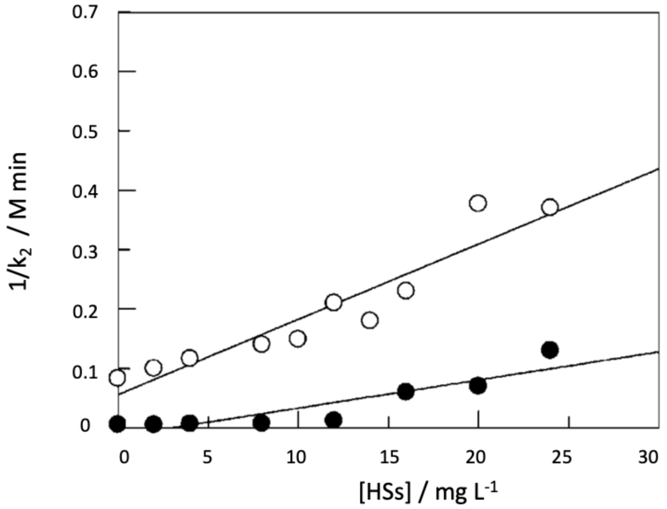


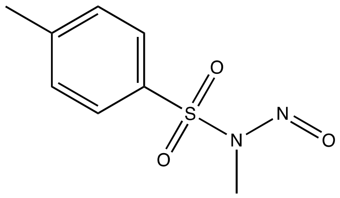
Figure 1.- Pseudophase model (eq 3) fit of experimental results for basic hydrolysis of CV (○) and MG (●) in the presence of humic aggregates. T=25ºC

Table 1.- Kinetic parameters of basic hydrolysis of carbocations in the presence of HSs aggregates obtained from the pseduphase model (eq. 1)

Substrate	k_w / M^{-1} min^{-1}	K_s mg^{-1}L
CV[51]	1.23±02	0.13±0.01
MG[51]	181±6	0.65±0.05

3. Hydrolysis of N-methyl-N-nitroso-p-toluene sulfonamide[54].

Another molecule of interest whose study was approached in our laboratory was N-methyl-N-nitroso-p-toluenesulfonamide (MNTS), which has biological interest because it is well known that nitrosulfonamides are very effective nitrosating agents[69]. Other advantage of this molecule the detailed research of our team of the mechanisms of its hydrolysis reactions (both acidic and basic) together with the mechanisms of the trans-nitrosation processes that involve it, both in homogeneous and microheterogeneous media[1–3,5,70–73]. 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 HS 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. With considerations like those applied for CV, and MG, we can propose a mechanism similar to that of the previous ionic compounds, such as the one shown in Scheme 3, so that, once again, the corresponding kinetic equation would be the equation 1 and the distribution of the MNTS would be governed by equation 2. From the adjustment of the experimental results to equation 1, a value for Ks = (25 ±2) mg^{-1}L was obtained (see figure 2).

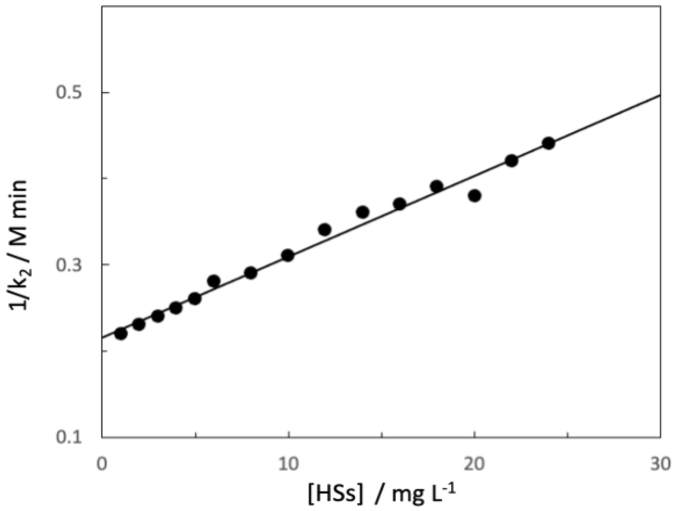
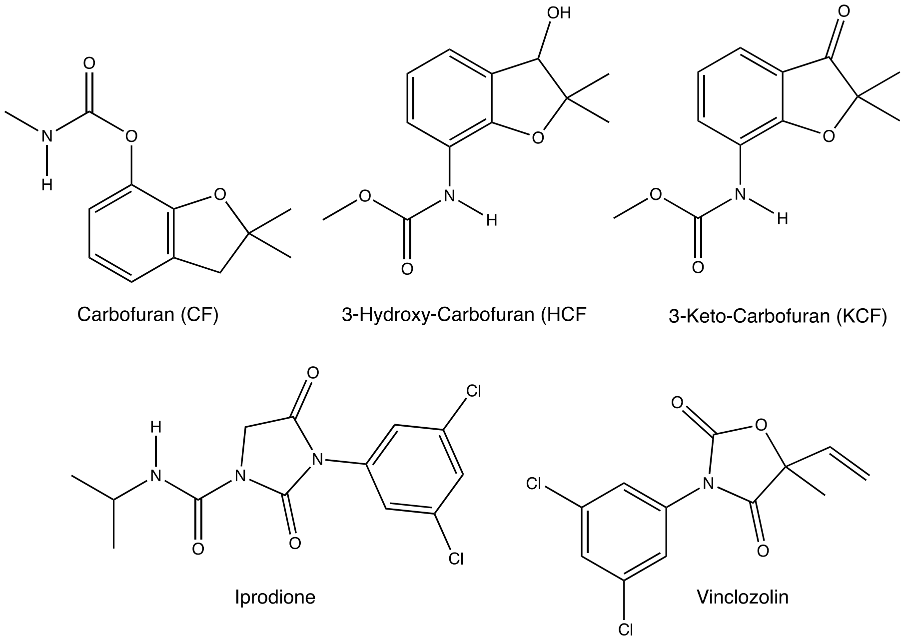


Figure 2.- Pseudophase model (eq 3) fit of experimental results for basic hydrolysis of MNTS in the presence of humic aggregates. T=25ºC

4. Hydrolysis of carbofuran and derivatives[53], iprodione[52] and vinclozolin[50].

In the previous results, it is shown that the comparability presented by the HSs aggregates have a kinetic behavior similar to the conventional micellar aggregates. With the study of the basic hydrolysis of both ionic substances (MG and CV)[51] 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) and two derivatives of carbofuran - 3-hydroxy-carbofuran (HCF) and 3-keto-carbofuran (KCF) -, as well as iprodione (IP) and vinclozolin (VI) in the presence of HSs, was analyzed and their behavior was compared with similar results in ionic and non-ionic micelles. Scheme 5 shows the xenobiotics under study.



Scheme 5: Carbofuran and carbofuran derivatives, iprodione and vinclozolin

In the case of carbamates, a curious behavior was observed, since we found an inhibition on the basic hydrolysis of HCF[53] and KCF[53], 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) (eq. 1 and eq. 2) we obtain values of the constant in water of $k_w = (1.86\pm0.06)x10^2$ $M^{-1}min^{-1}$ and $k_w = (11.4\pm0.6)x10^3$ $M^{-1}min^{-1}$ and some values of association constants of $K_s = (1.0\pm0.1)x10^{-2}$ $mg^{-1}L$ and $K_s = (5\pm1)x10^{-3}$ mg-1L respectively for HCF and KCF. However, no effect is found on the reaction rate for CF[53] 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 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 psedúphase model (eq. 1)

Substrate	k_w / M^{-1} min^{-1}	K_s $mg^{-1}L$
CF[53]	$(0.66\pm0.06)x10^2$	0
HCF[53]	$(1.86\pm0.06)x10^2$	$(1.0\pm0.1)x10^{-2}$
KCF[53]	$(11.4\pm0.6)x10^3$	$(5\pm1)x10^{-3}$
IP[52]	$(1.878\ \pm0.006)x10^3$	$(1.40\ \pm0.1)x10^{-2}$
VI[50]	$(8.2\pm0.4)x10^2$	$(9.7\pm0.1)x10^{-2}$

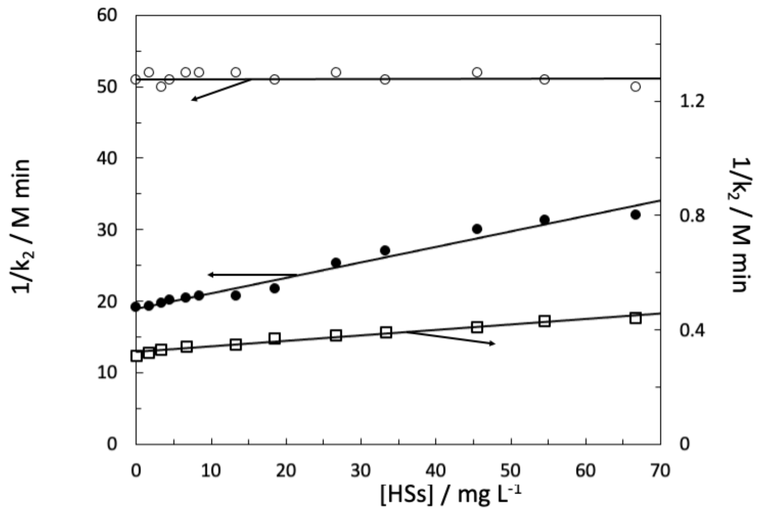


Figure 3.- Pseudophase model (eq 3) fit of experimental results for basic hydrolysis of CF (○), HCF (●) and KCF (☐) in the presence of humic aggregates. T=25ºC

When the basic hydrolysis of iprodione (IP)[52] was analyzed, an 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 of the previous cases. In the case of carbofuran-derivatives, an inhibition of -1.7 and 1.5 times-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 times-fold.

As in the previous cases, from Eq 1 we have obtained the corresponding kinetic parameters. A rate constant for the hydrolysis process in bulk water of $k_w = (1.878 \pm 0.006)x10^3$ M-1min-1 and an association constant to the addition of $K_s = (1.40 \pm 0.1)10^{-2}$ $mg^{-1}L$ (table 2). The higher value of the observed Ks would justify the greater inhibition observed on the hydrolysis of the PI compared to the carbofuran-derivatives.

Regarding the results obtained for the basic hydrolysis of vinclozolin (VI)[50], the inhibition observed due to the presence of HSs aggregates was much more dramatic, obtaining a decrease in the reaction rate of 9 times-fold. When the basic hydrolysis of iprodione (IP) was analyzed, an inhibition was also observed. By applying the pseudophase model and adjusting the experimental data to Eq 1, we obtain an association constant to the aggregate significantly higher than in the previous cases, $K_s = (9.7 \pm 0.1)x10^{-2}$ $mg^{-1}L$ (table 2). The greater affinity of the VI towards the HSs aggregates would be the cause of this greater 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 in order to evaluate the hydrophobicity of the HS core.

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 both aggregated HSs and normal micelles.

In the literature there are abundant studies that obtain the association constants of some of these compounds (MNTS[72,74–76] and CV[65,77]) to a large number of micelle aggregates, finding a linear correlation between Ks (MNTS) / Ks (CV) and the length of the hydrocarbon chain of traditional surfactants. Thus, the Ks (MNTS) / Ks (CV) ratio in the presence of HSs aggregates is 192. For the OTACl we find that Ks (MNTS) / Ks (CV) has a value of 10, that is, 19 times less than that found for HSs. In the case of SDS, the value of Ks (MNTS) / Ks (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.

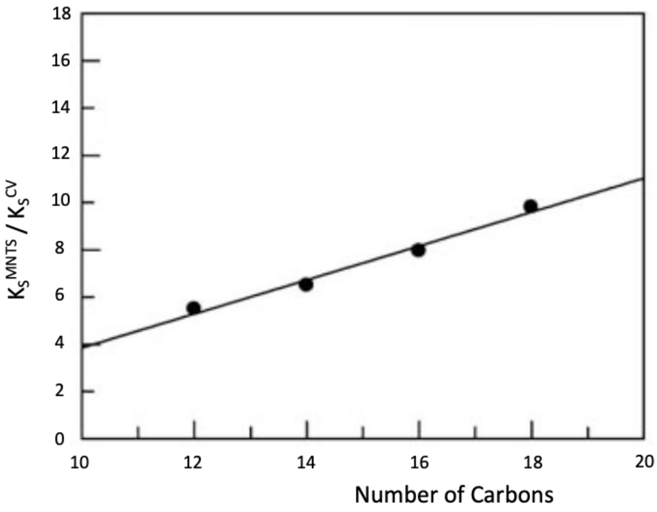


Figure 3.- Binding constants ratio between MNTS and CV to normal micelles as a function of the chain length of surfactants. T=25ºC

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 logP values of the substrates and the association constants found from the adjustment of the experimental data to the micellar pseudophase model (see figure 5).

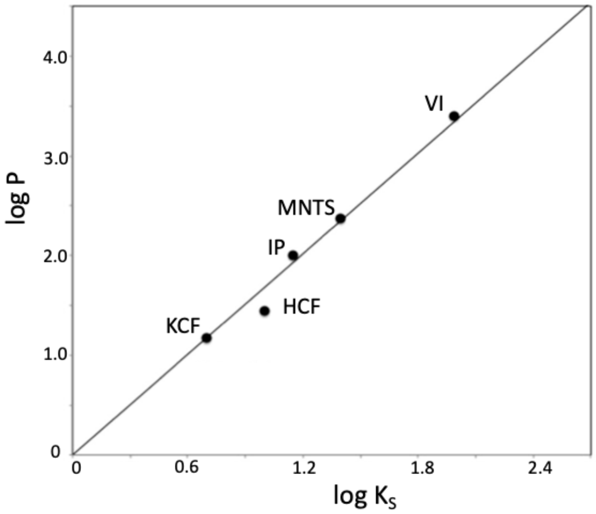


Figure 5.- Relationship between log Ks for different substrates in humic aggregates and the log P value for each substrate. T=25ºC

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 HO^- from the Stern layer of the aggregate due to the electrostatic interactions between the negative surface charge of the HSs and the HO^- ion. In this way, the inhibitions would be due to the inclusion of the different substrates inside micelles protecting them from nucleophilic attack by HO^-.

The fact that the hydrophilic / hydrophobic interactions are the main driving force behind the association of the different substrates to the aggregate has been demonstrate due to the evident correlation between the logP 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 alkylsulfate, alkyl trimethyl ammonium chloride. or alkyl pryridium chloride, even for hydrocarbon chains of more than 18 carbon atoms.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, J.C.M. and L.G-R.; resources, A.C. and A.S.; writing—original draft preparation, J.C.M. and A.C.; writing—review and editing, L.G-R. and J.C.M.; visualization, A.C. and A.S.; supervision, J.C.M.; project administration, J.C.M.; funding acquisition, L.G.R. and J.C.M. All authors have read and agreed to the published version of the manuscript."

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