



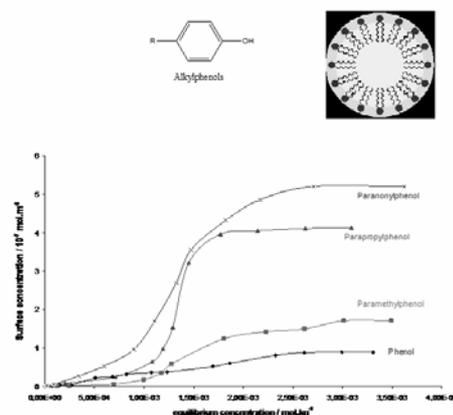
## ADSORPTION OF ALKYLPHENOLS ONTO GREEN CLAY SURFACE IN THE PRESENCE OF NONIONIC SURFACTANT

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Adsorption of alkylphenols onto green clay surface is studied by determining their adsorption isotherms separately than in the presence of various concentrations of the nonionic surfactant. When alone, alkylphenols are adsorbed with a mechanism close to that of surfactants. If the nonionic surfactant TX100 is added in the medium, the adsorbing properties are modified in a way that depends on the alkyl chain length. The longer the alkyl chain length of alkylphenol molecule the weakest is the influence of TX100 surface aggregates on their adsorption behaviour. This behaviour, may be due in a part to the adsorbing properties of the alkylphenols that are able to self-aggregate at the clay/water interface and in a part to the limited swelling capacity of the TX100 micelles or surface micelles. Partition coefficients between aqueous solution and surface aggregates are determined and compared to that calculated for bulk micelles.



### INTRODUCTION

In Europe, tons of nonionic surfactants are produced every year. A part of them are of the polyethoxyalkylphenol type. These compounds are biodegradable in water, but their biodegradation yields phenol and alkylphenol compounds that are persistent and toxic. In some cases, for instance the nonylphenol, they are considered as endocrine disruptors.<sup>1-5</sup> In the environment they may be related to reproductive and infertility problems in wildlife and bans and restrictions on their use has been associated with a reduction in health problems and the recovery of some wildlife populations. They may affect the reproductive

capacity of both animals and human being. It is then important to understand how alkylphenol compounds are fixed by the soil components and how they migrate. Because most of them have a very low solubility, it may be interesting to consider that their transportation in underground water as well as their fixation onto the soil components could be enhanced by their parent molecules (the nonionic surfactants) from which they are issued. This is why a study of the adsorption of alkylphenol compounds in the presence of nonionic surfactant is proposed here. Phenol, paramethyl, parapropyl and paranonylphenol are chosen as test molecules.

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Table 1

Physico-chemical properties of alkylphenols

Solute	MW / g mol <sup>-1</sup>	Solubility in water g L <sup>-1</sup> at 298 K	Log $k_{ow}$ * Octanol/water partition coefficient
Phenol	94.11	85	1.5
Paramethyphenol	108.13	19	1.97
Parapropylphenol	136.19	3	3.2
paranonylphenol	220.34	0.005	4.48

\*  $k_{o,w}$  is a concentration ratio.

Many studies have demonstrated that surfactant micelles greatly enhance the apparent solubility of hydrophobic organic compounds in water.<sup>6-10</sup>

For a given surfactant/solid couple and constant conditions of pH, ionic strength and temperature, the shape and the extent of these aggregates depend on the surfactant equilibrium concentration.<sup>11</sup>

The surfactant surface aggregates may solubilise hydrophobic molecules as bulk micelles do.<sup>12</sup>

The consequence may be an apparent enhancement of the adsorbed amount of the solute when a surfactant molecule is present in the system.

Partition coefficients were measured. The adsorption of the set of alkylphenols from aqueous solution onto green clay is first studied. Then their adsorption is studied in the presence of a nonionic surfactant of the polyethoxyalkylphenol type.

Adsorption isotherms were determined by the solution depletion method. The interactions between the molecules may be evidenced from the coadsorption isotherms.

## MATERIAL AND METHODS

The nonionic surfactant of the Triton set (TX100) was provided by Rhom and Haas. It contains more than 99% of surface-active compounds. TX100 is a parateroctylbenzene polyethoxy surfactant with a polydisperse polyethoxy chain having 9.5 ethoxy unit as an average. Its critical micelle concentration is 0.27 mmol.L<sup>-1</sup>. Phenol was provided by Aldrich; its purity is higher than 99%. The alkylphenols (paramethyl, parapropyl and paranonyl-) were provided by Aldrich and their purity is higher 99%. The solubility of these molecules in water is given in table 1, together with their octanol/water partition coefficient.

The green clay is a Tunisian sample. Its surface area in solution is 75 m<sup>2</sup> g<sup>-1</sup>, as determined by applying copper ethylene diamine adsorption isotherm at 298 K.<sup>13</sup>

The adsorption isotherms were determined by the solution depletion method. Solutions of known

concentration are poured inside 20 mL stoppered tubes together with the adsorbent. After equilibrium, the tubes are centrifuged and the supernatant is analysed. When the adsorption of a single molecule is studied (either phenol or surfactant), UV spectrometry is used to determine the equilibrium concentration. In the case of alkylphenol/surfactant mixtures, the following procedure was used. From the UV absorbance the total content of benzene groups was detected in the medium, whereas the concentration of phenol functions was derived from a specific reaction with the Folin Ciocalteu reactive.<sup>14-15</sup> The surfactant concentration is then determined by subtracting. In that aim, 0.5 mL of supernatant is mixed with 2.5 mL of the Folin Ciocalteu solution (0.1 mol L<sup>-1</sup>) containing Na<sub>2</sub>CO<sub>3</sub> at 75 g L<sup>-1</sup>. The mixture is heated at 50°C during 8 min and then quickly cooled down and refreshed in ice during 3 min. A complex is formed that can be titrated by visible spectrometry at 760 nm.

Calibration curves were first determined and it was also checked that there is no influence of the surfactant molecule on the titration of alkylphenols.

The CMC of alkylphenol/surfactant mixtures was deduced from the break of the surface tension versus log-surfactant concentration curve at constant alkylphenol concentration.

All experiments are done at 25°C and pH = 6.

## RESULTS AND DISCUSSION

Phenol, like alcohol, is only weakly adsorbed by oxide surfaces.<sup>16</sup> The reason is that water is preferentially adsorbed. The adsorption isotherms of phenol and alkylphenols onto green clay are presented in figure 1. The figure shows the amount of alkylphenol mole per area unit as a function of its concentration in solution at equilibrium. As already underlined, phenol has only a weak affinity for this type of surface. Its surface concentration at the plateau is 0.13 μmol m<sup>-2</sup>. The adsorption isotherm is L-shaped (Langmuir type). It means

that only a limited number of surface sites are adsorbing sites for the phenol molecule and that no effect of lateral interaction is visible between adsorbed molecules. The behaviour of the alkylphenols is totally different. They show S-shaped adsorption isotherms that are very similar to surfactant adsorption isotherms, for example the adsorption isotherm of TX100 onto the silica or kaolinite.<sup>17-19</sup>

Each of these adsorption isotherms presents a clear plateau that corresponds to a high surface concentration as compared with that of phenol.

This behaviour may be indicative of alkylphenol aggregation at the interface, as surfactants do. These molecules are not considered as surfactants<sup>20</sup> due to an unfavourable ratio of sizes of the hydrophilic and hydrophobic parts of the molecule, alkylphenols are not subject to micelle formation.

The interface may be also favourable for the accumulation of hydrophobic molecules.<sup>21, 22</sup>

The adsorption isotherms of alkylphenols in the presence of TX100 are plotted in figure 2 together with the evolution of the surface concentration of TX100.

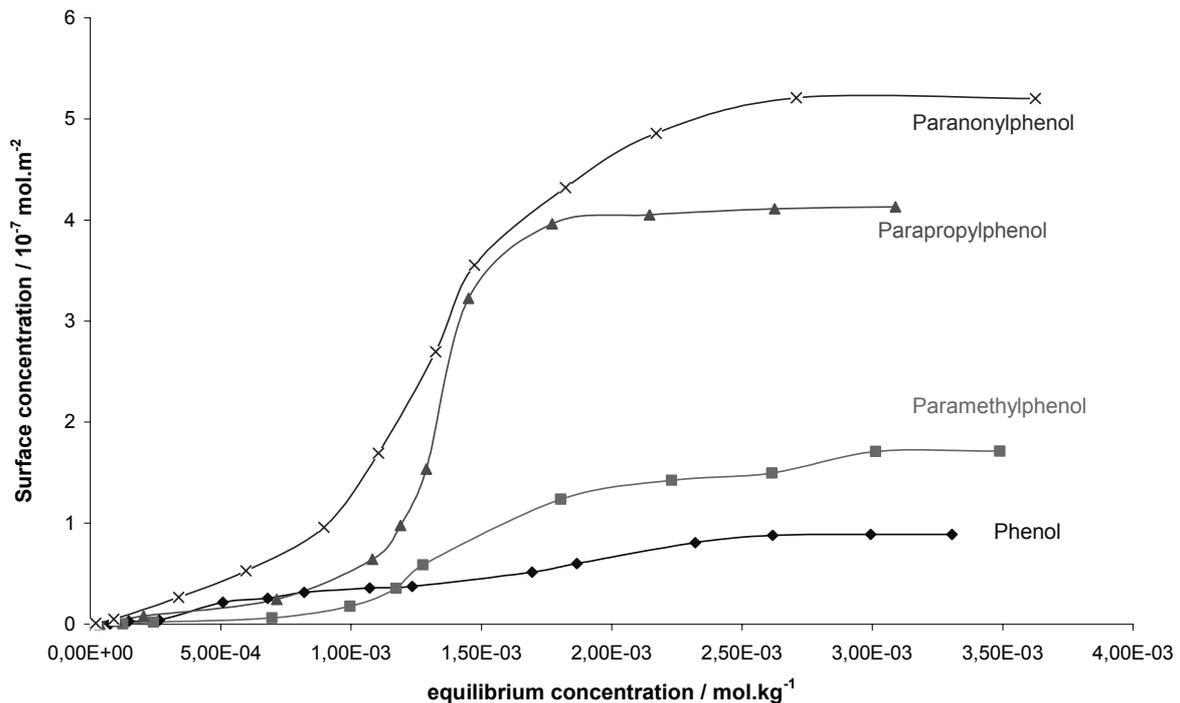


Fig. 1 – Adsorption isotherms of phenol and alkylphenols onto green clay.

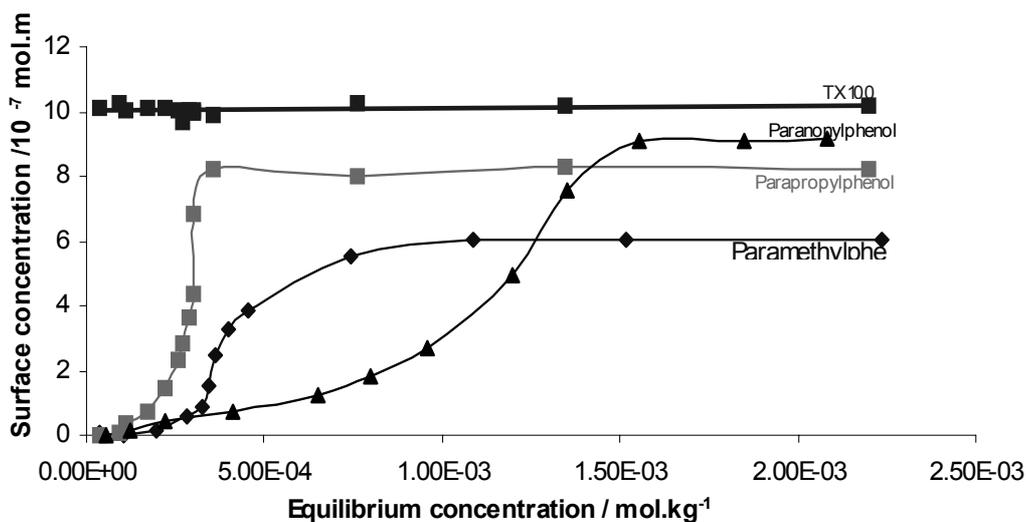


Fig. 2 – Adsorption isotherms of alkylphenols onto green clay with surfactant (▲: paranonylphenol, ■: parapropylphenol and ◆: paramethylphenol). The surface concentration of TX100 is also shown (by following form : ■).

Table 2

Critical micelle concentration of TX100 in the presence of alkylphenols. The CMC of TX100 alone is 0.27 mmol L<sup>-1</sup>. Partition coefficients of the alkylphenols between water and micelles  $K_m$  is calculated by equation (4) using  $\theta = 1$ , or water and admicelles  $K_{adm}$ .

Solute	Solute concentration mol L <sup>-1</sup>	CMC mmol L <sup>-1</sup>	$K_m$	$K_{adm}$
phenol	0.02	0.21	600	12700
P-methylphenol	0.02	0.19	820	8740
P-propylphenol	0.02	0.16	1130	6920
P-nonylphenol	$2 \cdot 10^{-5}$	0.14	$12 \times 10^5$	5990

The concentration of TX100 at equilibrium remains constant proving that the clay reaches its saturation on nonionic surfactant with a concentration of the order of  $10^{-6}$  mol.m<sup>-2</sup>.

Depending on the alkyl chain length, adsorption isotherm shape is differently modified by the presence of the nonionic surfactant.

The adsorption isotherm of parapropylphenol is the most strongly modified by the presence of the nonionic surfactant, the initial slope is very increased. For the paramethylphenol, the initial slope is increased, the step appears at a lower concentration and the plateau height is clearly increasing. Finally, for paranonylphenol, the step appears at almost the same concentration but a clear increase of the plateau surface concentration is observed.

A clear trend is observed: the longer the alkyl chain, the higher is the solute surface concentration without surfactant whereas the lower is the increase of solute surface concentration in the presence of surfactant. It means that the adsolubilisation efficiency is in the reverse order of the hydrophobic character of the molecules (as defined by their octanol/water partition coefficient given in table 1). This is the reverse of what it is generally observed.<sup>23-25</sup> This may be a size effect. The surface aggregates, as well as micelles, cannot swell indefinitely.

Another way to study the interaction between a hydrophobic solute and a surfactant molecule is to check its influence on the critical micelle concentration. The CMC determined from surface tension measurements are presented in table 2. The values of the solute concentration at which the CMC was determined is also given. The decrease of CMC due to the solute presence is in the order of hydrophobicity.

In order to compare the coadsorption mechanism to the solubilisation in micelles, it is interesting to compare the water/micelle and water/admicelle partition coefficients.

It is possible to calculate the partition coefficient of a solute between aqueous solution

and surface aggregates. On a molar fraction basis, this partition coefficient can be written:

$$K_{adm} = \frac{X_{adm}}{X_{aq}} \quad (1)$$

where  $X_{adm}$  is the molar fraction of solute inside surface aggregates and  $X_{aq}$  its molar fraction in aqueous solution.  $X_{adm}$  can be calculated from the surface concentrations of alkylphenol  $\Gamma(\text{alkylphenol})$  and surfactant  $\Gamma(\text{surf})$  by the following equation:

$$X_{adm} = \frac{\Gamma(\text{alkylphenol})}{\Gamma(\text{surf}) + \Gamma(\text{alkylphenol})} \quad (2)$$

where as  $X_{aq}$  is deduced from the alkylphenol equilibrium concentration  $C_{eq}$  by:

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \quad (3)$$

The micelle water partition coefficient is not easy to determine directly. Equations are proposed that deduce this partition coefficient from the CMC shift of the surfactant due to the hydrophobic solute. Nevertheless, such methods give results that can be different from experimental values.<sup>26, 27</sup>

The partition coefficient (on a molar fraction basis) derived from the CMC shift is given by the equation:<sup>27</sup>

$$K_m = 55.5 \left( \frac{\Delta CMC}{\Delta C_{eq}} \right) / \theta CMC^\circ \quad (4)$$

where  $\Delta CMC$  is the CMC shift for a given variation of the solute concentration  $\Delta C_{eq}$ ,  $\theta$  a parameter characteristic of the solute/surfactant pair and  $CMC^\circ$  is the surfactant CMC in the absence of solute.

The results of the calculated partition coefficients are given in table 2.

As often observed, the partition coefficients for admicelles are higher than for micelles excepted

for nonylphenol. The unexpected behaviour is the decrease of  $K_{adm}$  as a function of alkyl chain length. It would show that for the largest molecules the surface micelles are less efficient for solubilisation than bulk micelles. The surface may bring a constraint on the surface aggregates that may prevent them to swell as freely as bulk micelles.

## CONCLUSION

Green clay can adsorb alkylphenols with a mechanism close to that of surfactants. If a nonionic surfactant is added in the medium, the adsorbing properties are modified in a way that depends on the alkyl chain length. The longer the alkyl chain length of alkylphenol derivatives the lower is the influence of TX100 surface aggregates on their adsorption behaviour. The total capacity is increased in all cases. This unexpected behaviour, according to the relative hydrophobicity of the molecules, may be due in a part to the adsorbing properties of the alkylphenols that are able to aggregate alone at the green clay/water interface and in a part to the limited swelling capacity of the TX100 surface micelles.

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