



## Influence of Micellar Non-Ionic Surfactant Solutions in the Release of Sorbed Hydrophobic Polycyclic Aromatic Hydrocarbons in Soil Slurry

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In this study, we have investigated the efficiency of three micellar non-ionic surfactants in the solubilization of hydrophobic polycyclic aromatic hydrocarbons mainly, naphthalene, phenanthrene and pyrene. The non-ionic surfactants tested include the Tween 20, Tween 80 and Triton X-100. The critical micelle concentration (CMC) of all the surfactants was investigated by using a plot of surface tensions of surfactants *versus* log of their respective concentrations. The results show that Tween 80 performed better than the other three surfactants in the dissolution of polycyclic aromatic hydrocarbons. The gas chromatography coupled to a mass spectrometer was used for the separation and detection of the analytes.

**Key Words:** Non-ionic surfactants, Dissolution, Critical micelle concentration, Polycyclic aromatic hydrocarbons, GC-EI-MS.

### INTRODUCTION

The main challenge for the removal of organic hydrophobic contaminants in contaminated environments is the sorption of these contaminants to the soil, or sediment and bedrock surfaces. In this paper we report a technique to overcome this challenge by making these hydrophobic organic contaminants more available for extraction and/or other analytical treatment using traditional or conventional techniques. The non-ionic surfactants (Triton X-100, Tween 80 and Tween 20) were used to solubilize the sorbed organic contaminants and remove the surfactant using a selective liquid-liquid extraction technique. This selective desorption, was achieved successfully for a number of organic contaminants, mainly polycyclic aromatic hydrocarbons (PAHs). The use of surfactants in the solubilization and even remediation of contaminated environments (soils and sediments) is attractive because they are amphiphilic possessing both hydrophilic and hydrophobic moieties which allows them to accumulate at the interfaces of immiscible media and thus reduce the interfacial tension<sup>1</sup>.

The nonionic surfactants like any other surfactants have a tendency of assembling together to form aggregates and the concentration at which these aggregates begin to form is known as critical micelle concentration (CMC). Above this critical micelle concentration (CMC), surfactant monomers aggregate to form micelles spontaneously such that all the properties of matrix system are stabilized<sup>2</sup>.

The use of surfactants for removal/solubilization of organic hydrophobic pollutants in soils/sediments has more advantage than water alone. For instance surfactants have been reported to have the capability of removing one or two orders of magnitude more hydrophobic organics than water because of their ability to form microemulsions<sup>3</sup>. Nonionic surfactants such as Tween 80 (poly(oxyethylene)(20)-sorbitane mono-oleate) (Fig. 1b), are widely used surfactants for remediation applications because they are non-toxic<sup>4</sup>. The structures of the four surfactants used in this work are presented in Fig. 1b.

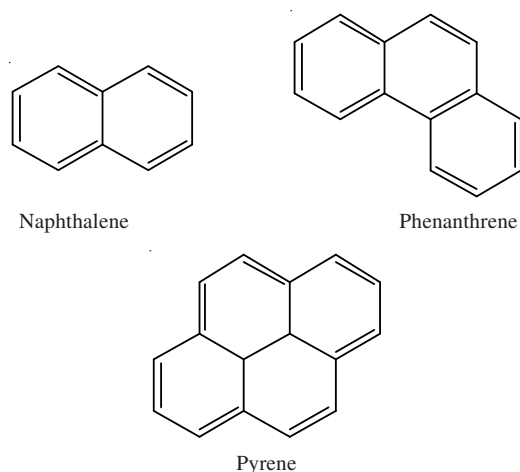


Fig. 1. (a) Chemical structure of the PAHs studied

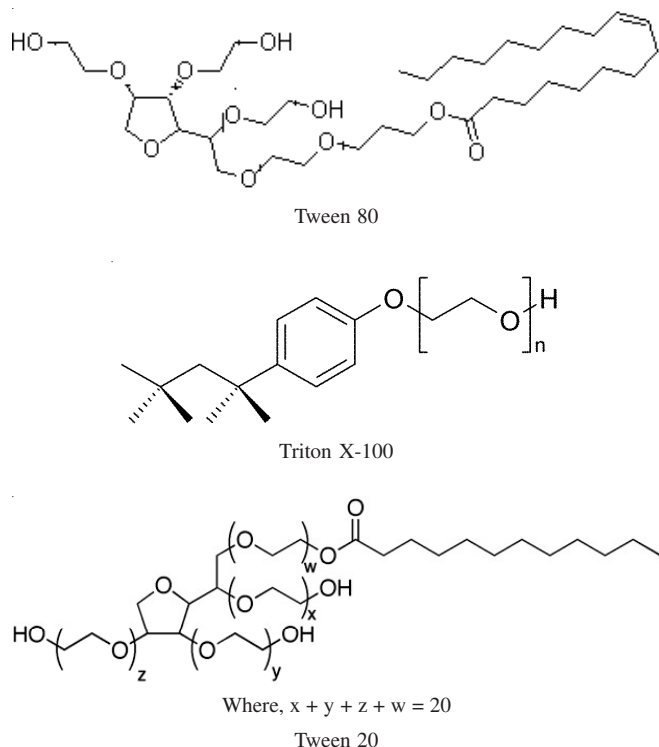


Fig. 1. (b) Chemical structures of the non ionic surfactants used in this work

## EXPERIMENTAL

The naphthalene, phenanthrene and pyrene standards (Fig. 1a) were purchased from Riedel-de-Haën (Seelze-Hannover, Germany). *n*-Hexane and toluene, calcium chloride were purchased from Panreac (Barcelona, Spain). Sodium hydroxide pellets (98 %) was obtained from Sarchem (Krugerdp, Africa), while, Tween 20, Tween 80 and triton x-100 (Fig. 1b) and hydrochloric acid were purchased from N.T. Laboratory Supplies, (Johannesburg, South Africa). A multicomponent working standard solution (1 µg/mL concentration of each compound) was prepared by appropriate dilutions of the stock solutions (1000 mg/L) with hexane:toluene (1:1) and stored under refrigeration (4 °C).

### Measurements of critical micelle concentration (CMC):

The determination of critical micelle concentration (CMC) for the surfactants was done by measuring their surface tensions using an OCA 20 LHT-SV equipment from Dataphysics (Raiffeisenstraße, Filderstadt, German) and the data was processed using CSA 20 software. The dispersive solid reference used was polyvinylidene, PVDF. Different concentrations of each surfactant were prepared and the surface tension measurements for each were taken. A plot of surface tension against log concentration s of each surfactant gave a measure of its corresponding CMC which was indicated at the point where the two plots meet.

**Optimization of various parameters:** For accuracy and precision of the results, various parameters were optimized. These include, the best ratio for surfactant:soil measured concentration, the critical micelle concentration and the sorption time.

**Gas chromatographic (GC-ECD) and gas chromatography-mass spectrometry (GC-EI-MS) analysis of MMLLE extracts:** HP Agilent 6890 GC/5973 MS (Santa Clara, CA

95051 USA) were both used for the analysis of PAHs. The column, J & W HP5-MS (30 m × 250 µm diameter × 0.25 µm film thickness) was employed in the separation of the polycyclic aromatic hydrocarbons. The flow rate of the carrier gas (nitrogen) was 1.5 mL/min and the injection volume was 0.5 mL. The glass liner was equipped with a plug of carbofrit (Resteck, Bellefonte, PA, USA). The mass spectrometer was operated under electron ionization (EI) mode, Scan 35-500 amu, Source 230 °C, Quad 150 °C and solvent delay 4 min.

## RESULTS AND DISCUSSION

### Measurements of critical micelle concentration (CMC):

Measurements of CMC were essential because of surfactants, many of their properties such as surface tension are very unpredictable when measured at points concentrations below CMC. To obtain more steady measures of surfactants' properties, the measurements have to be made at concentrations above CMC. In this work the surface tensions for the three surfactants, Tween 80, Tween 20 and Triton X-100 were measured by plotting the surface tension against the negative log concentrations of the surfactants. The CMC measurement was taken to be the point where these two graphs converge. Fig. 2a-c show that the results were then used to ensure that the working surfactant concentrations are actually above CMC.

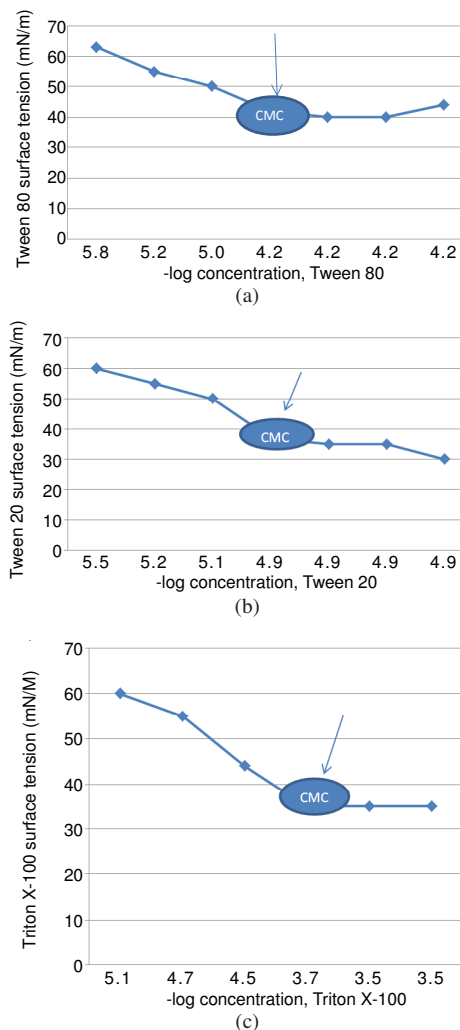


Fig. 2. (a) Measurements of CMC for Tween 80, (b) measurements of CMC for Tween 20, (c) measurements of CMC for Triton X-100

**Linearity tests and the dissolution kinetics of naphthalene on Tween-80:** In order to establish a linear range in the dissolution of naphthalene was chosen as it is relatively less hydrophobic and thus its linear range may be expected to be covering the range for the higher polycyclic aromatic hydrocarbons. Thus a kinetic study for the dissolution of naphthalene was performed using different concentrations of for a total time of 84 h and a control experiment was also included where no surfactant was added except the 0.01 M NaCl. Fig. 3a shows the kinetic curves of naphthalene were linear up to 36 h. This could be explained by the fact that, the soil pore structure might have been saturated and thus lost the capacity to adsorb more a scenario which cause a constant plateau on the graph. Therefore all the subsequent experiments were conducted within this linear range to ensure accuracy and precision of the recoveries. Furthermore, experiments to study the effect of concentration of the surfactant on the kinetics revealed similar linear relationship for studies that were performed using 0 % (no surfactant), up to 1500 mmol/kg of Tween 80 on the dissolution of naphthalene for 24 h each (Fig. 3b). This experiment was performed to optimize the concentration ratio of surfactant to soil weight ratio at optimum sorption time which is within the linearity zone. Results in Fig. 3b reveals that a concentration ratio of surfactant up to 1000 mmol/kg had linear response, thus this measure was used for all the subsequent sorption experiments.

**Sorption studies of surfactants onto the soil slurry:** The experimental set-up for sorption studies involved a sample soil:slurry, 1:40 (wt/v) and the slurry was made up of by 0.01 M NaCl in a surfactant. The experiments were performed at a series of surfactant concentrations each in duplicate and were incubated in a shaker for 24 h at room temperature. After shaking, slurry samples were centrifuged to remove the solids and the supernatant was analyzed for the sorption of surfactants in the soil slurry were worked out by calculating the difference between the initial and final concentrations.

**Sorption of surfactants onto the soil pore structure:** The results in Fig. 4 show that Triton X-100 had more sorption capabilities as compared to Tween 80 and Tween 20.

**Sorption of polycyclic aromatic hydrocarbons in soil-slurry medium:** The sorption studies related to polycyclic aromatic hydrocarbons in the soil-slurry medium was performed in two way, firstly the experiments involved polycyclic aromatic hydrocarbons without slurry and the second category involved polycyclic aromatic hydrocarbons in the presence of slurry (surfactant + 0.01 M NaCl). In all these cases, different concentrations of different polycyclic aromatic hydrocarbons were investigated and the experiments were performed in duplicate. The samples in the two categories were subjected to shaking for 24 h at room temperature and then centrifugation. The sorbed portion of polycyclic aromatic hydrocarbons was obtained by calculating the difference between the initial concentration of polycyclic aromatic hydrocarbons and the corresponding final concentrations. Fig. 5a-b, show the sorption results and Triton X-100 sorbed more polycyclic aromatic hydrocarbons than the Tween 80 and Tween 20. Triton X performed better followed by Tween 80 and then Tween 20. This could be due to the molecular structures of these surfactants which gave different chemistry in terms of penetrating

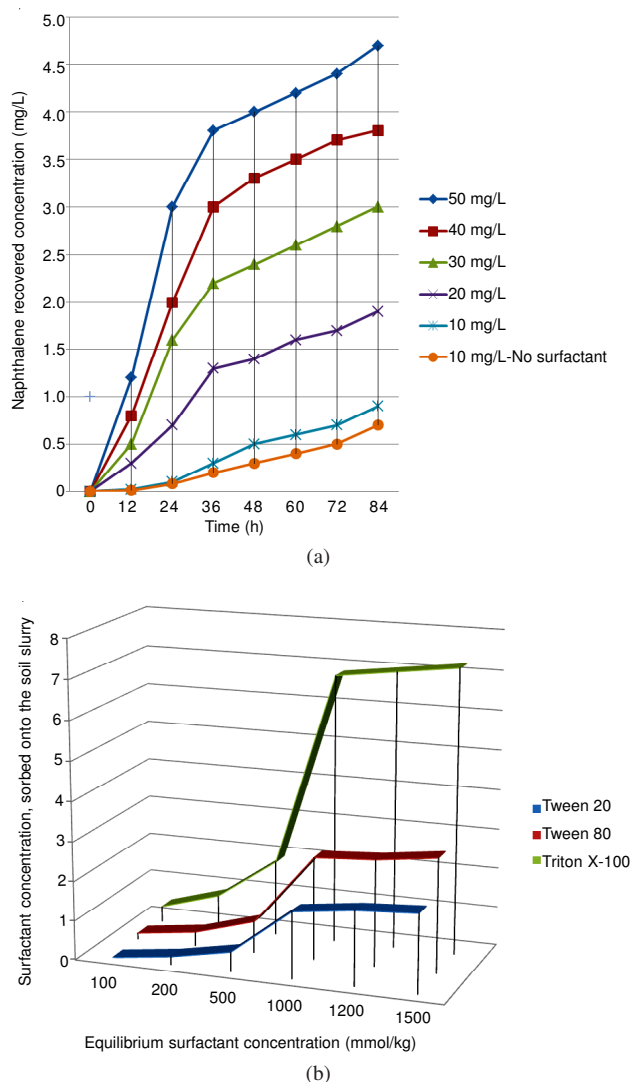


Fig. 3. (a) Kinetic study of the dissolution of naphthalene in Tween 80 surfactant (b) Surfactant penetration onto the soil structure

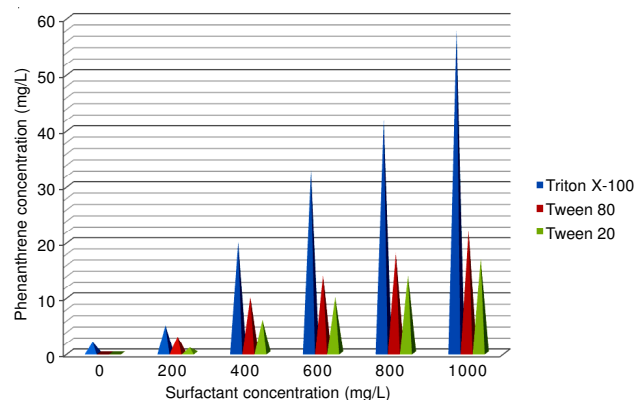


Fig. 4. Sorption of surfactants onto the soil pore structure

the soil pore structures and idea which can be supported also by the trend observed in Fig. 3b. Another observation that is clear from the results is that naphthalene sorbed more than phenanthrene and other polycyclic aromatic hydrocarbons studied. This trend suggests that the sorption was inversely proportional to hydrophobicity, the more the hydrophobic the compound the less it is sorbed, when considering similar experimental conditions.

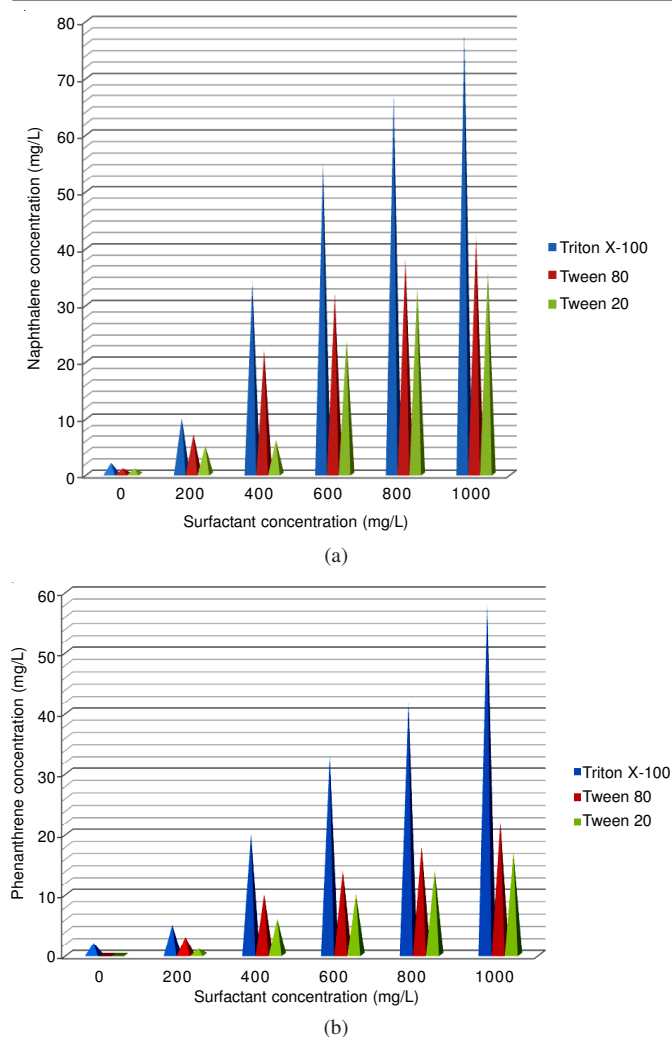


Fig. 5. (a) Sorption of naphthalene by surfactants, (b) Sorption of phenanthrene by surfactants

**Separation and detection of polycyclic aromatic hydrocarbons by GC-EI-MS:** The gas chromatographic separation polycyclic aromatic hydrocarbons was successfully achieved and the identification of the individual peaks were aided and validated by the MS which was equipped with NIST98 library. Fig. 6, shows a clean spectrum of pyrene from the sample sorbed using Triton X-100.

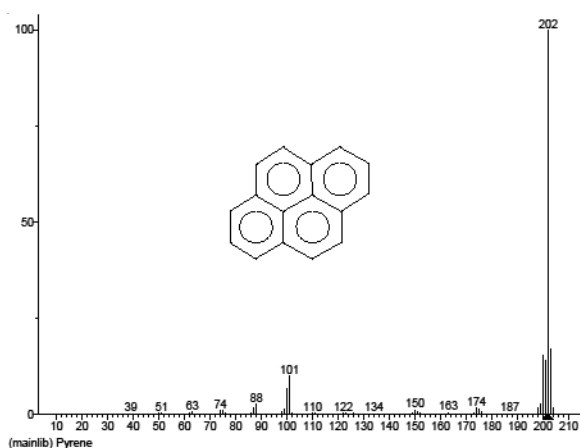


Fig. 6. Mass spectrum for pyrene from the triton X-100 sorbed slurry sample

## Conclusion

The use of surfactants has shown potential in the solubilization of polycyclic aromatic hydrocarbons and that the micelles formed increased the polycyclic aromatic hydrocarbons removal rate. The mobilization of surfactants assisted the creation of low interfacial tensions between the hydrophobic organic polycyclic aromatic hydrocarbons and the water which helped the release of polycyclic aromatic hydrocarbons from the soil pores. The inclusion of the non-ionic surfactants has shown the capability to enhance the solubilisation of the organic hydrophobic pollutants such as polycyclic aromatic hydrocarbons. This approach has the potential to improve the extent of the availability of such hydrophobic pollutants for the remediation strategies of the contaminated environments. Triton X-100 gave the highest solubilisation effects followed by Tween 80 and then Tween 20. Moreover the trend of sorption showed to be inversely proportional to the hydrophobicity of the polycyclic aromatic hydrocarbon studied.

## ACKNOWLEDGEMENTS

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