Experimental report

19/06/2020

Proposal: **9-10-1588** **Council:** 10/2018

Title: SANS studies on the structures of non-ionic surfactant micelles with/without solubilised pesticide and waxes

Research area: Biology

This proposal is a new proposal

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Samples: C12E6
C12E12
Cyprodinil
C28H58O

Instrument	Requested days	Allocated days	From	To
D11	3	0		
D33	3	2	29/07/2019	31/07/2019

Abstract:

The promotion of pesticide uptake into plant leaves has been a hot topic for decades in agriculture due to its profound influence on crop production and environmental protection. To promote pesticide uptake, surfactants are widely used in pesticidal formulation by enhancing pesticide solubility and mobility. Upon applying agri-spraying, its first contact is the most outer surface of plants, which is a waxy layer. It is essential to understand how surfactants along with bioactive ingredients interacting with waxes. Our previous SANS investigation revealed that the shape of the non-ionic micelles saturated with pesticide typically changed from round sphere to rod-like structure. In this process, the length of the aggregates expanded greatly whilst the shell shrank and became dehydrated. In spite of extensive research on surfactant-pesticide interaction, relevant knowledge about surfactant-pesticide-wax interaction still remains sparse. Thus, we intend to use SANS to look at the changes of micellar structure with/without saturated pesticide before and after wax solubilisation.

SANS studies on the structures of non-ionic surfactant micelles with/without solubilised pesticide and waxes

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Experimental objective

SANS is about the only technique that can determine the size and shape of surfactant micelles and the subsequent changes upon pesticide and plant wax solubilisation. The aim of this work is first to understand how the micellar structures of non-ionic $C_{12}E_6$ surfactants are affected by pesticide solubilisation and further wax solubilisation. Understanding these molecular processes is important to pesticide formulation. Partially deuterated surfactants have been used to improve the sensitivity and resolution essential for unravelling the structural details in the multicomponent micellar systems.

Results and discussion

We performed some continuous SANS investigation on the interaction of waxes and non-ionic surfactant $C_{12}E_6$ with/without solubilised pesticides as well. A series of SANS runs were performed to study the micellar structures of $C_{12}E_6$ solubilised with/without a typical fungicide, cyprodinil (CP) interacting with waxes. Measurements including $C_{12}E_6$ with wax and $C_{12}E_6$ with CP and waxes were performed in three contrasts ($dC_{12}hE_6$, $hC_{12}dE_6$ and $hC_{12}hE_6$) at 20°C in D_2O. The results were fitted into a core-shell cylinder model. In this model, as shown in Figure 1, the micelle was simplified as a cylinder consisting of an inner core of tails and outer shell of heads. The major parameters are: core radius (R core), core length (L core), micellar total length (L total), shell thickness (T shell), core SLD, shell SLD and solvent SLD.

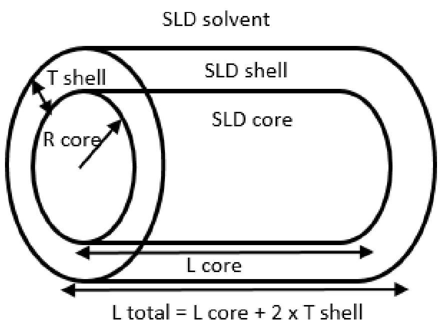

Figure 1: the core shell cylinder model and its major parameters.

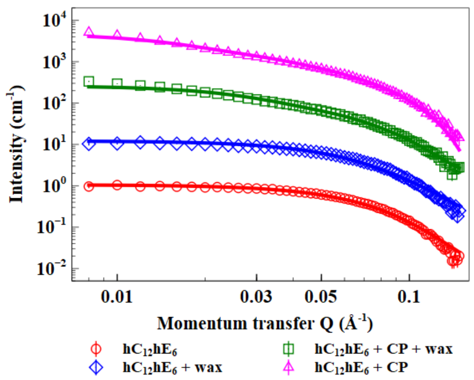

Figure 2: the SANS profiles for h-$C_{12}E_6$ with solubilised pesticides and waxes along with their best fits (solid lines). ○ $hC_{12}hE_6$, ◊ $hC_{12}hE_6$+wax x10, □ $hC_{12}hE_6$+CP+wax x100, △ $hC_{12}hE_6$+CP x1000.

	Core Radius /Å	Shell thickness /Å	Micellar total length /Å	Aggregation number	Shell hydration /%
$C_{12}E_6$	16.0 ± 0.5	11.0 ± 0.5	82 ± 6	132 ± 6	68 ± 2
$C_{12}E_6$ + wax	16.0 ± 0.5	11 ± 0.5	98 ± 6	185 ± 15	64 ± 2
$C_{12}E_6$ + CP + wax	16.0 ± 0.5	10 ± 1	160 ± 10	320 ± 25	47 ± 2
$C_{12}E_6$ + CP	16.0 ± 0.5	9.0 ± 1.0	330 ± 20	735 ± 30	38 ± 2

Table 1: the best fitted parameters from measured SANS profiles.

Figure 2 depicts the SANS results for $hC_{12}hE_6$ with solubilised pesticides and waxes along with their best fits. The Q range was from 0.008 to 0.15 $Å^{-1}$ as the background was cut (SANS profiles were separated by multiplying constants for clear display). The detailed fitting parameters are presented in Table 1.

Our results clearly revealed that the waxes could be solubilised into micelle but no significant change of the micellar structure was observed. When waxes were dissolved into the micelle which was pre-saturated with pesticides, the micellar length decreased greatly and the shell hydrated. The micelle structure had a trend to return back to bare $C_{12}E_6$ micelle structure. This implies that the CP was released from the micelle whilst the waxes were dissolved into micelle. Further investigations including NMR and DLS measurements will focus on the boundary changes of $C_{12}E_6$ with pesticides and waxes and the solubility of pesticides and waxes in the micelles to give us better understanding on the interaction mechanism.

LIKELY OUTCOMES FROM EXPERIMENT

The results have been discussed in an internal meeting between Syngenta and the University of Manchester. We believe this study has paved a new path for bridging our knowledge from colloidal science to agrichemical formulation. The results will be also likely used as thesis data and journal publication.