ESRF	**Experiment title:** Evaluation of micellar transitions in gemini cationic surfactants	**Experiment number**: CH-2250
Beamline: BM26B	**Date of experiment**: from: 22 September 2006 to: 25 September 2006	**Date of report**: 28 February 2007
Shifts: 9	**Local contact(s)**: Dr. Giuseppe Portale	*Received at ESRF:*

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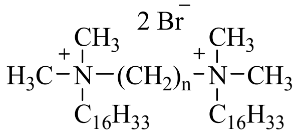
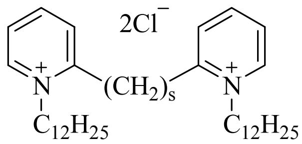
Report:

During our experiment at the beamline BM26B (experiment CH-2250) we studied two series of gemini surfactants having quaternary ammonium headgroups (**I,** 16-n-16 2Br) and pyridinium headgroups (**II**):



n=3, 4, 6, 10, 12

I

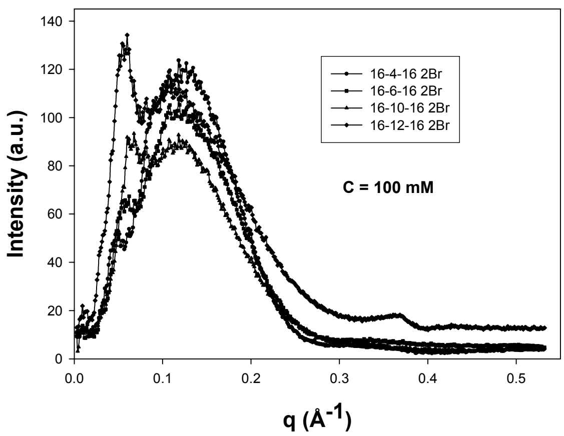


s=3, 4, 8, 12

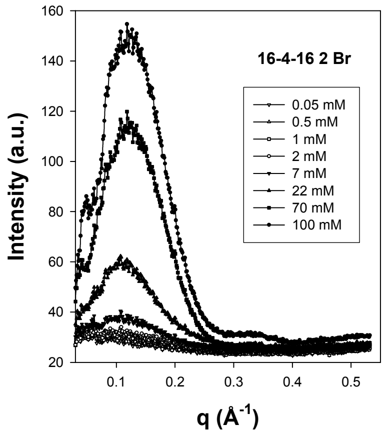
II

The aim of this experiment is to demonstrate the propensity of this series of surfactants to give micellar transformations, i.e. the occurrence of different micellar shapes as a function of the concentration and of the spacer length. As a preliminar study we performed several measurements by conductivity, steady-state fluorescence technique, using different probes such as pyrene, coumarin 6 (C6), and fluorescein. The use of different probes enabled us to detect the cmc and to evidence the formation of premicellar aggregates. Besides, we performed fluorescence quenching measurements by using the 1-(3-sulfopropyl)-6-methoxyquinolinium (SPQ)[1] as a probe, giving access to the cmc, the degree of micellar ionisation and the second cmc (due to micellar shape transitions).
Concerning the SAXS experiments, we performed measurements at different concentrations for every surfactant of the series. Measurements at different pH were planned as stated on the proposal, but they were not performed, due to an instrumental failure during the last two shifts.
Following the results of our SPQ fluorescence measurements, we defined the appropriate concentration range to be considered for SAXS measurements and decided to perform more than 4 measurements for each concentration. We investigated the following concentrations for compound 16-4-16 2Br (**I**, n =4): 0.05, 0.5,

1, 2, 7, 22, 70 and 100 mM, because of its particular good behaviour in mesoporous silicas materials preparation.[2] The other compounds of the 16-n-16 2Br series (**I**, n = 3, 6, 10 and 12) were studied in the concentration range 0.05 - 100 mM. All the measurements were performed in a liquid cell with mica windows and a Teflon spacer of 3mm at 25°C, working with two sample to detector distances (1.5 m and 7.5 m) to access a large *q* range ($5*10^{-3} < Q < 0.5$ Å^{-1}). The effect of temperature was checked for 16-3-16 2Br by measuring also at 35°C. The observed SAXS peaks give clear indication of structural transformations in the micelles, in agreement with preliminary results. We are confident in obtaining reliable data to determine the "so-called" aggregation number, i.e. the number of surfactant molecules that compose a single micelle and we expect this number to change abruptly when a micellar shape transition occurs. To our knowledge, no details on the aggregation numbers were extracted until now with SAXS measurements.
We are currently working on the analysis of SAXS data of different concentration of 16-4-16 2Br (see Figure on the right) and a manuscript is in preparation. Data concerning 16-4-16 2Br are giving very important information about micelles formation and their structural changes. By using the SPQ fluorescence, we were able to detect three transitions: the first at $2.5*10^{-5}$ M concerning the formation of micelles with spheroidal shape.[3] A second transition at $8*10^{-5}$ M is ascribed to a spheroidal to rod-like transition, which is in agreement with literature data.[4] The third transition is observed at 15 mM and suggests the formation of open membranes or ellipsoidal micelles as observed by other research groups by different techniques.[5,6] The combination of our results with literature data can enable us to perform a better data treatment and a correct choice of the suitable structure factors. The SAXS peak intensity increases when the surfactant concentration is increased and these results seem to agree with literature data and with the SPQ preliminary experiments. We are also going to elaborate data concerning other spacers, for which the following plot (left hand side) shows different behaviour and probably different micellar shape, depending on the spacer length.



Figures: SAXS data measured at RT on: left) gemini with different spacer length and right) 16-4-16 2Br at different concentrations



Moreover, we tested two of these surfactants (**I**, n = 4, 12) to synthesise mesoporous silicas materials with different structure: MCM-41 and MCM-48. The results obtained are currently under study and another manuscript is in preparation.
During our 9 beamtime shifts, we also tried to perform further studies concerning a different series of surfactants having pyridinium headgroups (**II**). Our intention was to study all these surfactants of different spacer length at different concentrations as we performed for surfactants **I**. We had planned an experiment including 4 different concentrations ranging from 1 to 100 mM for the four spacers but unfortunately we only could perform an experiment concerning compound **II** having s = 3, with a sample to detector distance of 7.5 m, due to instrumental problem which caused our experiments at the beamline to be stopped. However the few preliminar results were encouraging for a possible future investigation.

Reference List

1. Kuwamoto, K.; Asakawa, T.; Ohta, A.; Miyagishi, S. *Langmuir* **2005,** *21*, 7691-7695.
2. Gianotti, E.; Berlier, G.; Costabello, K.; Coluccia, S.; Meneau, F. *Catal. Today,* in press.
3. Pisarcik, M.; Dubnickova, M.; Devinsky, F.; Lacko, I.; Skvarla, J. *Colloids Surf. A: Physicochemical and Engineering Aspects* **1998,** *143*, 69-75.
4. Aswal, V. K.; De, S.; Goyal, P. S.; Bhattacharya, S.; Heenan, R. K. *Phys. Rew. E* **1998,** *57*, 776-783.
5. Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995,** *11*, 1448-1456.
6. De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. *J. Phys. Chem.* **1996,** *100*, 11664-11671.