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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title:	**Experiment**
ESRF	Studying the Kinteics of Interaction of Silica Nanoparticles with vesicles	**number**: SC 4165

Beamline: ID02	**Date of experiment**: from:27.02.2016 to:29.02.2016	**Date of report**: 20.6.2016
Shifts:	**Local contact(s)**: Sylvain Prévost	*Received at ESRF:*

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Report:

The question of the detailed mechanism of adhesion of SiNPs and polymer grafted SiO_2@PDMAEMA-NPs to vesicle membranes is to be resolved by means of coupling the stopped-flow technique with SAXS, where the vesicle dispersions are rapidly mixed with the corresponding NP solution. This allows following subsequent structural changes with ms time resolution for instance the formation of decorated vesicles or of bigger agglomerates. For this purpose we employed dioleylphospatidylcholine (DOPC) vesicles with a radius of ~50 or 400 nm (obtained by extrusion), which have a form factor minimum around $q = 0.035$ nm^{-1}. The most relevant q range then was 0.01-0.5 nm. This very low q is important to see whether during the process larger agglomerates are formed as decorated vesicles. The short time range, where fast adhesion to the vesicles occurs (decoration; $\tau_{ch} = 10$ ms-10 s) will be studied with correspondingly higher time resolution up to 10 s. We always employed DOPC vesicles at pH = 7.4 and they will be mixed with SiNPs and cationic polymer grafted SiO_2@PDMAEMA-NP of core diameter 15 or 55 nm in order to see how their size affects the adhesion scenario. As another parameter we controlled the interaction potential between membrane and NPs by variation of the membrane charge. This was done by employing vesicles where 2 and 10 mol% of DOPC were substituted by anionic 1,2-Dimyristoyl-sn-glycero-3-phosphatidic acid sodium salt (DMPA), thereby introducing a systematic repulsion between the membrane and the anionic SiNPs or systematic attraction of SiO_2@PDMAEMA-NPs.

First we compared the initial final state of those systems observing that there is no difference between initial and final state for pure NPs with vesicle (uncharged or charged), so we skipped further stopped flow experiments for those systems (figure 1). In contrary SAXS-data of SiO_2@PDMAEMA ($R_H = 42$ nm) and corresponding vesicle NP mixture differ from each other where a time altering intensity increase in the low q-range can be observed for the vesicle-NP mixture. Depending on NP size all data show a first intensity minima at $q = 0.16801$ nm^{-1} for SiO_2@PDMAEMA- and SiO_2-NP and at $q = 0.18822$ nm^{-1} and $q = 0.503$ nm^{-1} confirming the presence of NPs core with a mean core radius of 26.4 nm and 8.3 nm respectively. As mentioned before scattering data of SiO_2@PDMAEMA-vesicle mixtures show an altering intensity increase compared to

scattering data of pure NPs thus we expecting the formation of larger aggregates probably as decorated vesicles. In principel from the ratio of the forward scattering I_0 compared to that of the SiO$_2$@PDMAEMA-NPs we can calculate the aggregation number N_{agg} of NPs for one vesicle but the measured q-range is too small and not all data reach a plateau. The expected I_0 should be 10 times higher at $q = 0.001$ nm^{-1} (calculated from equation 1) so we only can estimate I_0 value for initial and final state of those mixtures to estimate N_{agg} (table 1 and 2). Due to an altering intensity increase for SiO$_2$@PDMAEMA-vesicle mixture we decided to study the vesicle surface charge density (tunable with DMPA content) and also the [NP]/[Ves]-ratio as parameter.
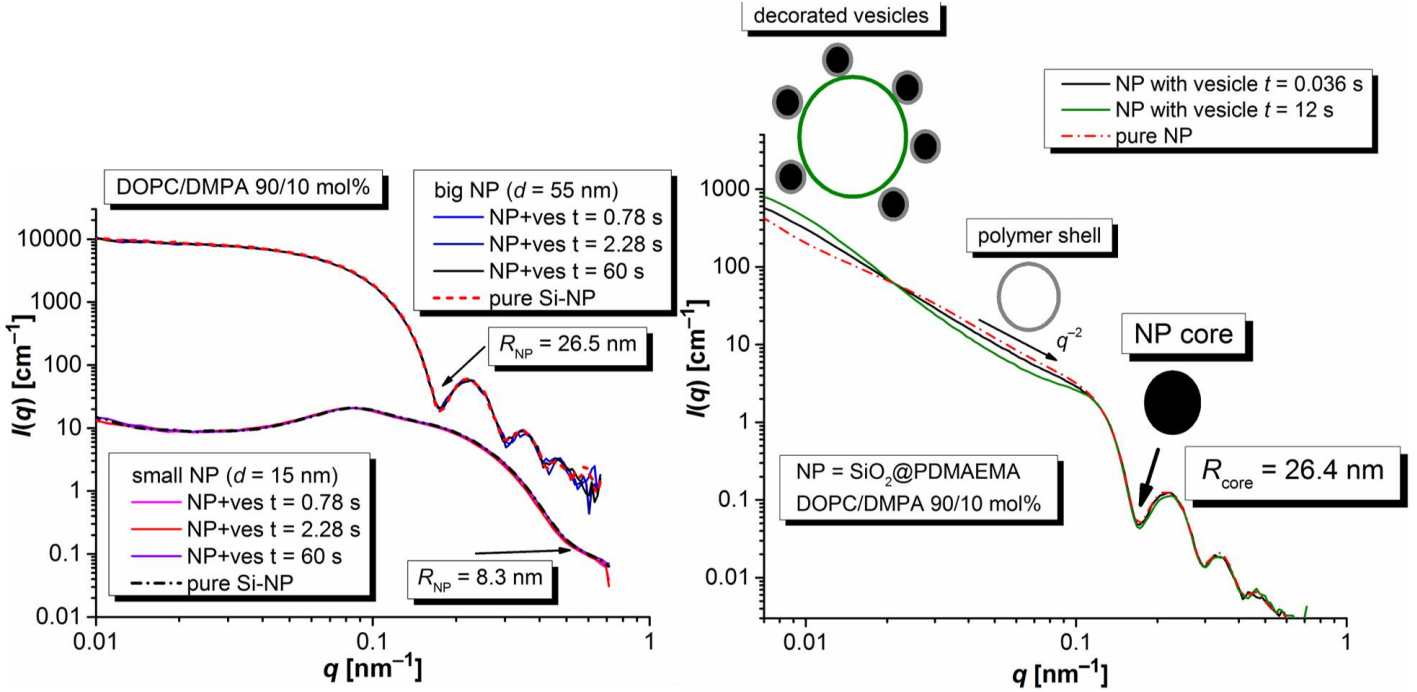

Figure 1: Shown are example of pure NPs and NP-vesicle mixtures for initial and final state: Left: SiO$_2$-NPs with two different core radii and vesicle sizes; right: SiO$_2$@PDMAEMA-NPs. For a better comparison single scattering data are not multiplied with a factor

Table 1: measured and estimated values for the Intensity and N_{agg} estimation for DOPC/DMPA 98/2 mol%

[NP]/[Ves]	I($q = 6.6*10^{-3}$ nm) [cm^{-1}] initial state (data)	I($q = 6.6*10^{-3}$ nm) [cm^{-1}] final state (Data)	I_0 [cm^{-1}] initial state (approximated)	I_0 [cm^{-1}] final state (approximated)	N_{agg}
8.8	452	835	600	9000	15
5.5	462	702	1020	8000	7.84
4.1	400	625	1200	6500	5.42
1.9	492	720	980	4000	4.08
1.5	325	410	800	3500	4.38
1.2	225	327	780	3200	4.10
0.6	202	257	500	3000	6.0

Table 2: measured and estimated values for the Intensity and N_{agg} estimation for DOPC/DMPA 90/10 mol%

[NP]/[Ves]	I($q = 6.6*10^{-3}$ nm) [cm^{-1}] initial state (data)	I($q = 6.6*10^{-3}$ nm) [cm^{-1}] final state (Data)	I_0 [cm^{-1}] initial state (approximated)	I_0 [cm^{-1}] final state (approximated)	N_{agg}
32.3	300	800	480	800	1.67
14.7	512	1198	816	10000	12.25
8.8	608	842	960	9000	9.375
5.9	490	728	784	7000	8.93
4.1	403	600	640	5500	8.59
2.9	390	525	624	3200	5.13
1.3	252	321	400	2800	7.00
1.0	180	220	288	2000	6.94
0.6	61	121	96	1000	10.42
0.3	42	63	64	60	0.94

For describing the intensity increase at $q = 6.6*10^{-3}$ nm^{-1} we used a simple exponential fit given as:

$$I(t) = I_0 * exp\left(\frac{t}{\tau_{decay}}\right) + I_{end} \qquad\qquad \textit{Equation 1}$$

I_0 is the intensity at the dead time, I_{end} the intensity when reached the equilibrium, τ_{decay} the relaxation time and t the time in s.
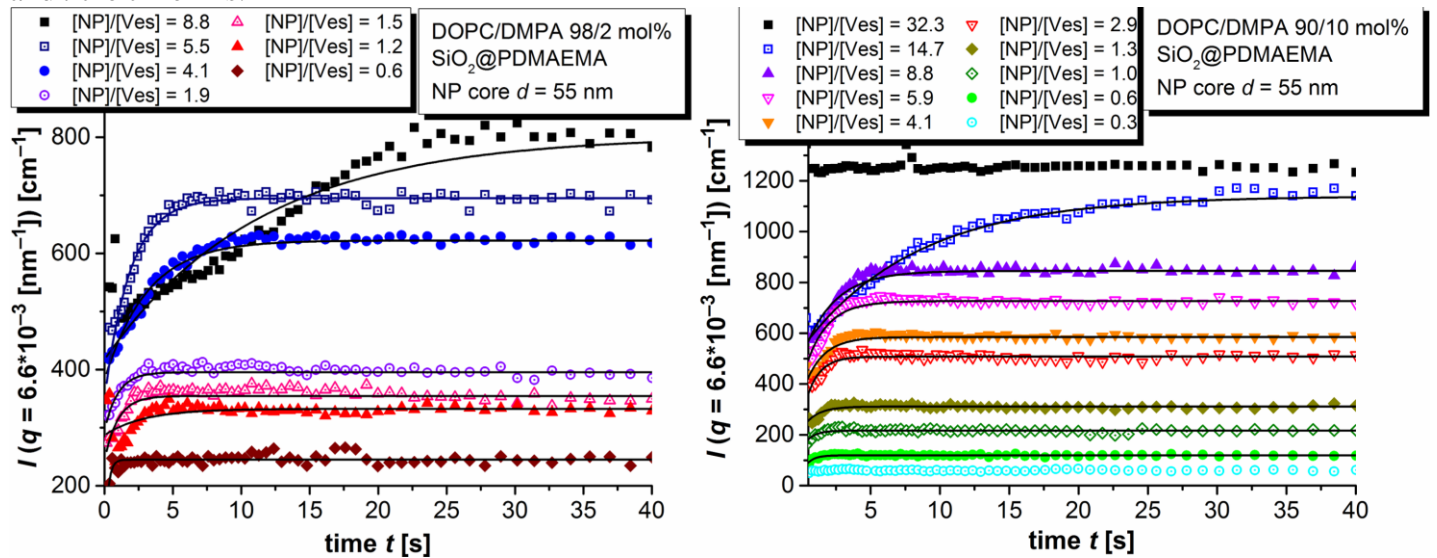

Figure 2: Shown are intensity $I(q)$ [cm^{-1}] versus time [s] at a constant q value of $q = 6.6*10^{-3}$ nm^{-1} for SiO$_2$@PDMAEMA-NP with different charged vesicles: Left: DOPC/DMPA 98/2 mol %; right: DOPC/DMPA 90/10 mol%

For anionic vesicles (DMPA = 2 or 10 %) an increasing [NP]/[Ves]-ratio leads to longer relaxation times of the vesicle NP-system and with a too high or low [NP]/[Ves]-ratios no interaction behavior can be observed. Interestingly one would expect a quicker relaxation process with increasing NP amount but we observe totaly different results. This we may interpret such that immediately after mixing of anionic vesicles with cationic SiO$_2$@PDMAEMA-NP a quick formation of decorated vesicles begins with a netto charge reversal from anionic vesicles to cationic decorated vesicles results. This subsequently shields additional SiO$_2$@PDMAEMA-NPs from further adsorption and those mixture needs longer for relaxation. Assuming that each monomer unit of SiO$_2$@PDMAEMA is positively charged, we may estimate the maximum number of charges per particle to be ~26400. Comparing this value with the maximal amount of counter charges per one vesicle (18625 for DOPC/DMPA 90/10 mol%) shows us that in principal a small amount of NPs is enough for a charge conversion. One has to keep in mind, that the real charge ratio per vesicle or NP is quiet smaller due surrounding counter ions, non the less only the detaching NP area with vesicle surface neutralizes the charge.
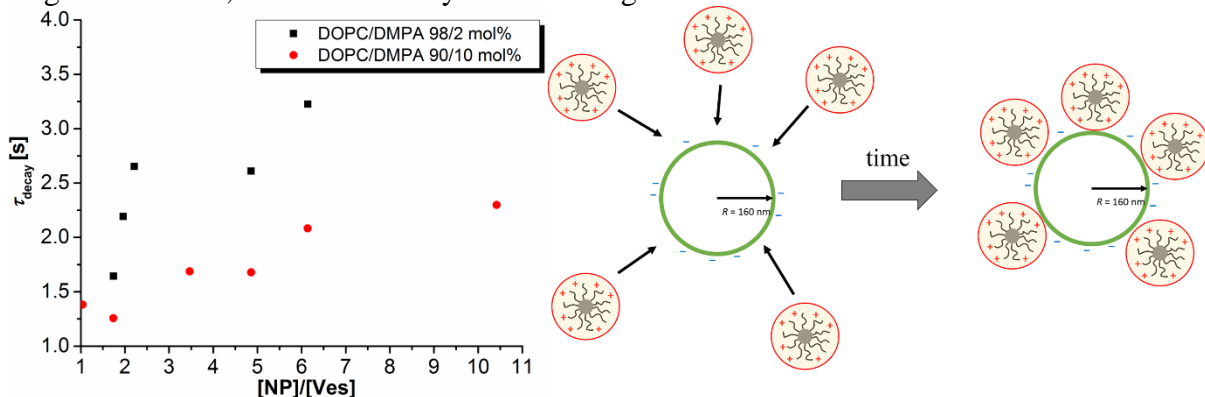

Figure 3: Shown is τ_{decay} versus the [NP]/[Ves]-ratio for both charged vesicles

Comparing τ_{decay} values at same ratios as a function of the vesicle charged density those values are generally higher for lower DMPA content and thus a longer relaxation times can be observed for less charged vesicles. Typically, a higher charge results in stronger attractive interaction between NPs and vesicles and thus to quicker adsorption. In general, our experiment sheds a lot of light onto the interesting and important interactions between nanoparticles and vesicles and how these are governed by the electrostatic conditions between them. These results will be a solid basis for further experiments in that direction that will substantially enhance our understanding of such complex systems.