ESRF	**Experiment title:** In situ SAXS/USAXS investigation of homogeneous and heterogeneous nucleation in a nanoparticle jet produced by Rapid Expansion of Supercritical Fluids	**Experiment number**: ME864
Beamline: ID02	**Date of experiment**: from: 22.09.2004 to: 25.09.2004	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Pierre Panine	*Received at ESRF:*

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Experiment Report ME864

Introduction

In September 2004 we carried out first experiments for the in situ interrogation of particle formation in a RESS jet. At the ESRF beamline ID02, nine shifts of beamtime were granted from 22-25.09.2004 for proposal ME864. Aim of this first measurement campaign was to test and prove the feasibilty of resolving particle sizes in a highly diluted and weakly scattering system. From former measurements performed with LIF technique [1] we were expecting volume fractions in the jet of about 10^{-7}.

Experimental

A schematic representation of the apparatus is shown in **Fig.1**. This apparatus is designed for experiments in the temperature range from 270 to 370 K and pressures up to p=250bar. Pure CO_2 is condensed from a solvent reservoir (60 bar) into the thermostatic extraction unit (high-pressure cell (5), V=500ml, with basket insert (4)) at T=270K. Heating the liquid CO_2 to the desired supercritical temperature pressurizes the system up to 22MPa. Thereby the supercritical solvent is loaded with the solute and thermal equilibrium is reached usually within 15 minutes. Thereafter, pure CO_2 flows through the bypass section of the extraction unit (2) and the capillary nozzle (1) to minimize the unsteadiness of the flow and to accelerate thermal equilibrium. After equilibrium, the valve (3) at the top of the high-pressure cell is carefully opened and the supercritical solution (CO_2 and solute) flows through the thermostated duct to the capillary nozzle (50µm diameter). By adjusting the temperature of the high-pressure cell the pressure is maintained above 18-20 MPa for about 10-15 minutes, providing a jet of conical shape with widths of 0.05-2 mm, lengths of 0.5-5mm (**Fig.2**).

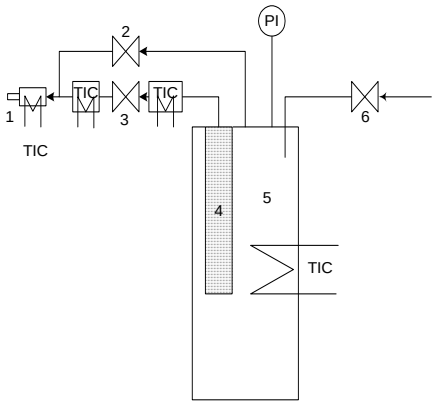

Fig. 1: ***The mobile RESS batch reactor***

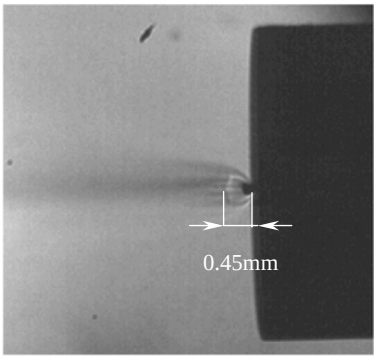

Fig. 2: ***Schlieren picture of the jet***

The setup, as described above was installed in the experiment hutch as can be seen in Fig.3. Experiments were performed with two different solutes (Benzoic acid, $Cu(TMHD)_2$) and as well with pure CO_2, using the pinhole setup of the high brilliance beamline ID02. Table 1 summarises the experiment conditions during this campaign. The x-ray beam position was centered with respect to the jet axis (SAX = 0)

During the first experiments the expected stability of the jet over a period of several minutes was not always given due to a clogged nozzle and ducting. Nevertheless it was decided to perform as many measurements as possible.

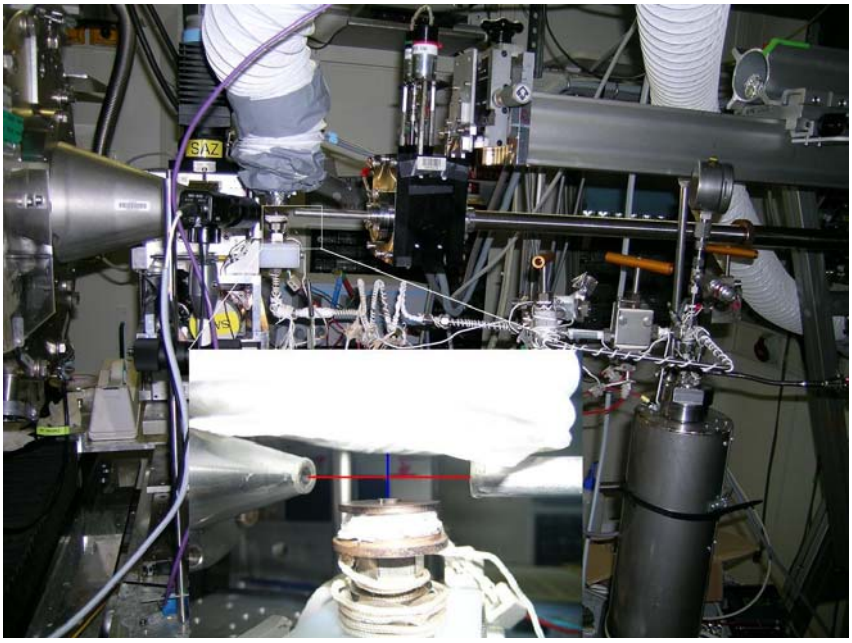

Figure 3RESS batch setup in the experiment hutch with details of the heated nozzle. The red line indicates the position of the x-ray beam, the blue line the position of the jet from a 50 µm nozzle. The pressurised and heated extractor is the cylinder visible on the right side

Experiment No.	CO_2-02	CO_2-03	Cu-01	Cu-02	Cu-02-1	Cu-03	Ben-00	Ben-01	Ben-02	Ben-03	Ben-05
Solvent	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2
Solute	-	-	A	A	A	A	B	B	B	B	B
Initial Extraction pressure (After valve opening) [bar]	240 (200)	240 (200)	215 (180)	205 (180)	205 (180)	205 (180)	240 (200)	240 (200)	240 (200)	240 (200)	260 (210)
Extraction Temperature at experiment start [ºC]	45	58	50	41.5	41	41.5	55	55	60	55	55
Nozzle temperature [ºC]	80	78	63	70	70	76	80	80	80	80	80
Radial SAXS beam position [mm] (radial=0)	1	1.3	0.7	1	1	1	1	0.9	0.9	0.9	1.3

Table 1 Experiment conditions fo all experiment runs. Solute A = $Cu(TMHD)_2$,,solute B = Benzoic acid.

Results

Fig.4 shows some exemplary SAXS measurements for Benzoic acid/CO_2, $Cu(THMD)_2$/CO_2 and pure CO_2. Graph **A** and **B** show as well a fit on the first averaged measurements. A global unified scattering function was used [2], assuming spherical geometry as the SEM picture suggests in graph **D**. The quality of the fit is reasonably good. However, for high q the consistency is less good. A fit in these regions is hampered by the degraded quality of the signal. As a first evaluation, these fits would yield a primary radius of 26.6nm and a polydispersity index (PDI= $BR_g^4/(1.62G)$) of 25.29 for benzoic acid, for the copper complex a primary radius of 26.34nm and a PDI of 24.5 respectively. The radii obtained are in good agreement with LIF measurements which yielded particle radii of about 27nm 1mm centered above the nozzle for benzoic acid [1].

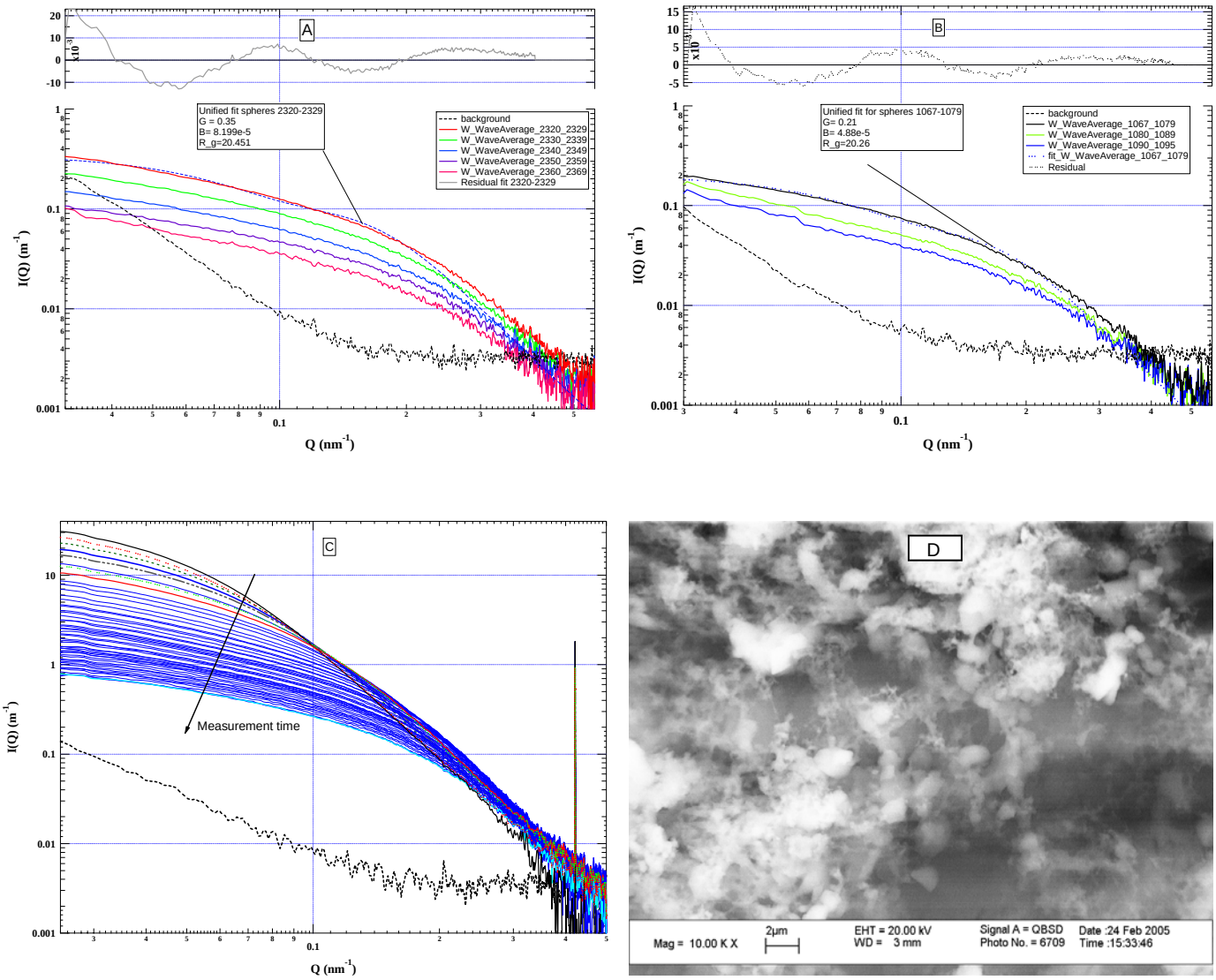

*Figure 4 Background corrected log-log plots of small angle scattering at ID02 of A) CO_2/Benzoic acid, B) CO_2/ $Cu(TMHD)_2$ C) pure CO_2 at different times. Radial (x) and axial (z) position in the jet: x= 0mm, z=1mm, initial extraction pressure p=240 (CO_2, benzoic acid) and p=210 (Cu-complex) bar, nozzle temperatures 70-80C. For **A)** and **B)** each curve is averaged over consecutive 0.5s measurements, the residual of the fit from the first averaged I(q) is shown in the top part of the graphs. The black dotted lines represent the background intensities. **C)** depicts single measurements for pure CO_2 without fit. **D)** shows a FE-SEM picture of the copper complex($Cu(THMD)_2$) collected with a needle inserted in the jet some mm from the nozzle exit. SEM chamber pressure was limited to p=10Pa min. due to the vapour pressure of the complex.*

Graph **C** shows a set of measurements of pure CO_2 at the same position and with similar P and T. Applied to the scattering curves of pure CO_2, the fit on the initial measurements would result in a radius of 50nm and a PDI of 6.3 for the last recorded measurement a radius of 29.4nm and a PDI of 24.9. The values for the first measurement is in good aggreement with earlier simulations on pure CO_2 jets [3].

It is very likely that the two phase region and the solid line of CO_2 has been crossed, creating droplets and ice, with a relatively high concentration, yielding a high signal (N.B, with pure CO_2 as a comparatively "weak" scatterer). A difference in photon flux can not explain this high signal (on PIN 42, before start of measurement, 1.6 10^{12} ph/s for pure CO_2, 1.7 and 1.9 10^{12} ph/s for benzoic acid and the copper complex).

With the solutes on the other hand, the jet was much less visible suggesting that we expanded directly from supercritical into gas, only having solute particles with a lower concentration on one side, on the other side being hampered with the problem of clogging. This resulted in a smaller jet, lower concentrations and hence a lower signal.

Summary

The measurement time granted to our team allowed us to prove the feasibilty of in situ SAXS measurements on a highly diluted nanoparticle jet from the RESS process. Due to the geometry of our setup we encountered regular problems with clogging, both of the nozzle and the ducting between the extractor and the nozzle. The flexible tubing linking the nozzle on the translation stage with the extractor was most likely the reason for this. The relatively long ducting together with diameter changes led to increased pressure drop and hence premature nucleation. The intention to subtract the signal from the pure CO_2 gas could not be implemented, since we did not manage to obtain a CO_2 gas jet at exactly the same conditions as for the jet with solutes.
In addition some problems were encountered with the windows of the SAXS pinhole setup, leading to a corruption of some measurements.
We intend to improve this setup by either using a bigger batch extractor or a continuous working extractor which is fed directly via a membrane pump and thermostat from a gas bottle, this being situated outside the experiment hutch. This should enable us to have a better temporal stability of the jet, together with a optimised link between the extractor and the nozzle, avoiding blockage of the latter.
We would like to thank especially Dr. Pierre Panine from ESRF for his support and guidance on the operation of the SAXS beamline, as well as Dr. Jan Kunert (ESA) and Dipl.-Ing. Martin Steurenthaler (ITTK) for the support during the execution of the experiments.

References

[1] Final Report: Forschungsvorhaben 2270 „Herstellung submikroner organischer Partikel aus überkritischer Lösung und deren zweidimensionale laserspektroskopische Charakterisierung“ (Production of submicron organic particles using supercritical fluids and their two dimensional laserspectroscopic characterisation) http://www.dechema.de/data/dechemaneu_/mbf/2270.pdf (in german)

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