



	Experiment title: Investigation of Structural Pathways in the Solubilisation Process in Amphiphilic Systems	Experiment number: SC 1385
Beamline: ID02	Date of experiment: from: 14. 4. 2004 to: 17. 4. 2004	Date of report:
Shifts: 9	Local contact(s): Dr. Thomas WEISS	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Michael GRADZIELSKI* Ekramun NABI Dieter GRÄBNER* Lehrstuhl für Physikalische Chemie I, Universität Bayreuth, D-95440 Bayreuth, Germany Markus BURKHARDT* Lehrstuhl für Makromolekulare Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany		

Report:

The equilibrium conditions for the solubilisation of oils into amphiphilic systems have been studied in much detail in recent years [1]. In contrast, much less is known about the dynamics of solubilisation processes, despite the fact that they are of central importance for many applications, e. g. in cosmetics, pharmaceutical formulations, or detergency [2]. A powerful tool to study the dynamics of such morphological transitions is the coupling of the stopped-flow method to small-angle scattering detection [3].

In order to gain insight into the dynamics of oil solubilisation in micellar solutions and microemulsions we performed stopped-flow experiments in which either oil was mixed with a surfactant solution (thereby forming a microemulsion) or in which a micellar solution was mixed with a microemulsion (thereby probing the oil exchange between microemulsion droplets and micelles), both composed of the same surfactant. For that purpose we employed the zwitterionic surfactant tetradecyldimethylamine oxide (TDMAO) or the nonionic surfactant pentaoxyethylene dodecyl monoether ($C_{12}E_5$) as typical representatives for microemulsion forming surfactants.

As an example for such an experiments in fig. 1 scattering curves are given for the case where an aqueous solution of 50 mM $C_{12}E_5$ is mixed with 50 mM $C_{12}E_5$ /120 mM dodecane, a process, where large microemulsion droplets are transformed into smaller microemulsion droplets by the presence of the added surfactant. This process was followed with exposure

times of 20 ms and one can discern very nicely the structural changes that take place within the first 200 ms until for longer times the scattering pattern of equilibrated solutions of 50 mM $C_{12}E_5$ /60 mM dodecane are recovered. The obtained scattering curves can be fitted with a model where originally a mixture of short elongated micelles and large microemulsion droplets are present which is transformed into one population of microemulsion droplets of intermediate size. In fig. 2 the mean size of the microemulsion droplets is given as a function of time (for simplicity the part originally aggregated in micelles is not shown here). It is evident that a fast equilibration process with a characteristic time of 110 ms is followed by a slower process in which the aggregates grow again of a time constant of 850 ms.

Similar experiments were done for octane, dodecane, toluene, ethylbenzene, and hexylacetate as oils, thereby covering a large range of polarity of the solubilised oil. These experiments showed generically similar behaviour and can be analysed in the same fashion, but the time scales involved depend on the type of oil involved being faster for short chain oils and slower for longer ones. In addition it is interesting to note that for the hexylacetate at higher concentrations the formation of elongated particles takes place at intermediate concentrations.

In summary it should be noted that this sort of exchange dynamics of hydrophobic solutes is not easily followed by other techniques and especially detailed structural information regarding the aggregates present at intermediate stages can only be obtained by these time-resolved SAXS experiments. Our experiments could clearly show that there is a correlation between the type of oil in the microemulsions and its exchange dynamics as well as the formation dynamics of the corresponding microemulsion.

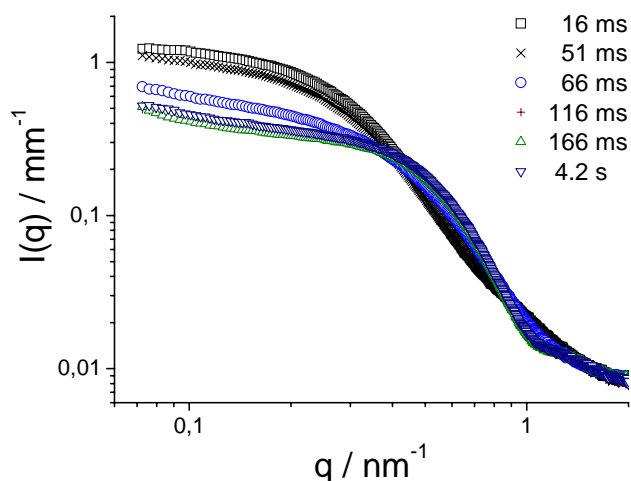


Fig. 1: SAXS intensity curves for various times after mixing 50 mM $C_{12}E_5$ are mixed with 50 mM $C_{12}E_5$ /120 mM dodecane

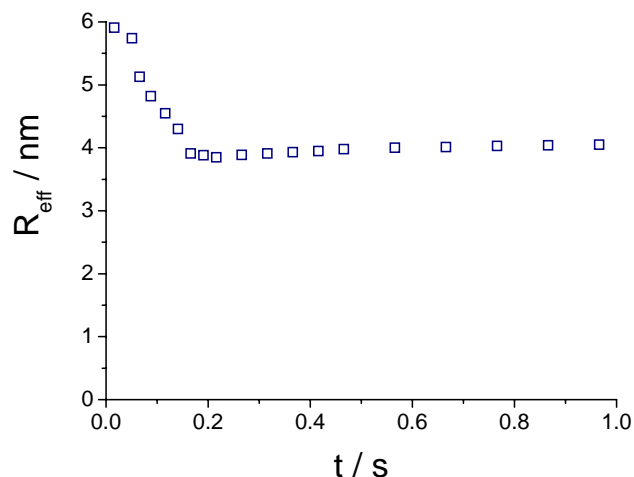


Fig. 2: Change of effective size of the microemulsion aggregates of the mixing shown in fig. 1 as a function of time.

- [1] Laughlin R G *The aqueous phase behavior of surfactants* 1994 (Academic Press: London, San Diego)
- [2] Tadros Th. F. *Applied Surfactants* 2005 (Wiley-VCH: Weinheim)
- [3] Schmölzer S, Gräbner D, Gradzielski M and Narayanan T 2002 *Phys. Rev. Lett* **88** 258301