Experimental Report

04/04/2014

Proposal: **9-10-1302** **Council:** 10/2012

Title: Unexpected enormous efficiency increase of fluorinated CO_2-microemulisons by the addtion of non-amphiphilic hydrophobic additives

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: H_2O, D_2O, NaCl, CO_2, C_6H_{12}, C_6D_{12}, flourinated non-ionic surfactants

Instrument	Req. Days	All. Days	From	To
D11	3	2	05/04/2013	07/04/2013

Abstract:

Microemulsions containing supercritical CO_2 have attracted much attention as novel environmental friendly solvents or as templates for nanoporous foams.However,using the Principle of Supercritical Microemulsion Expansion,the foams suffer from aging phenomena,resulting in pore sizes in the lower µm range.In order to suppress the aging of the pores an anti-aging concept was developed.Expanding supercritical microemulsions containing low-molecular hydrophobic molecules,these additives are supposed to accumulate at the blowing agent/matrix interface reducing the interfacial tensions and therewith the aging of the pores.Surprisingly,phase behavior studies showed that adding only small amounts of C_6H_{12} improve the efficiency of fluorinated non-ionic surfactants by a factor of 2.Assuming a non-homogeneous distribution of CO_2 and C_6H_{12} in the sub-domains would explain this enormous effect.To investigate the role of C_6H_{12} and its distribution in the scCO_2/additive sub-domain we propose systematic contrast variation measurements on the system H_2O/D_2O/NaCl – CO_2/C_6H_{12}/C_6D_{12} – fluorinated non-ionic surfactant mixture the contrast can be adjusted by both the H_2O/D_2O and C_6H_{12}/C_6D_{12}-ratio.

Unexpected enormous efficiency increase of fluorinated CO2-microemulisons by the addition of non-amphiphilic hydrophobic additives

Report on Experiment No: 9-10-1302

Abstract: Microemulsions containing near- or supercritical CO_2 ($scCO_2$) have attracted much attention in the past years as novel environmental friendly solvents in the field of green chemistry or as templates for nanoporous foams. However, using the Principle of Supercritical Microemulsion Expansion (POSME) [1], the foams suffer from aging phenomena, resulting in pore sizes in the lower micrometer range. In order to suppress the aging of the pores an anti-aging concept was developed [2]. Expanding near- or supercritical microemulsions containing low-molecular hydrophobic molecules, these additives are supposed to accumulate at the blowing agent/matrix interface reducing the interfacial tensions and therewith the aging of the pores. Surprisingly, phase behavior studies showed that the addition of only small amounts of cyclohexane improve the efficiency of fluorinated non-ionic surfactants to solubilize water and supercritical CO_2 by a factor of two. Assuming a non-homogeneous distribution of CO_2 and cyclohexane in the sub-domains would explain this enormous effect. In order to investigate the role of the additive and its distribution in the hydrophobic ($scCO_2$/additive) sub-domain we performed systematic contrast variation measurements. Studying microemulsions of the type H_2O/D_2O/NaCl – CO_2/cyclohexane-d12/cyclohexane-h12 – fluorinated non-ionic surfactant the contrast can be adjusted by both the H_2O/D_2O and C_6H_{12}/C_6D_{12}-ratio. Using the GIFT procedure to determine the scattering length density distribution the analysis of the scattering data clearly shows that the scattering length density profiles differ considerably from $scCO_2$-microemulsions without cyclohexane [3]. Instead of a nearly constant scattering length density, a density profile that varies systematically over half of the droplet radius was detected. Thus, the hypothesis of the formation of depletion zone of cyclohexane close to the fluorinated amphiphilic film could clearly be proven.

SANS measurements: To determine the scattering length density of the fluorinated surfactants we performed a contrast variation on the stock solution of H_2O/D_2O and 8% fluorinated surfactants ($\gamma_a = 0.08$). Subsequently, we performed a systematic contrast variation on microemulsions of the type H_2O/D_2O/NaCl – CO_2/cyclohexane-d12/cyclohexane-h12 with a concentration of cyclohexane of 20% within the hydrophobic phase. The mass fraction of hydrophobic substance in the overall mixture was kept at a constant value of $w_B = 0.1$. By choosing a temperature of 20°C, which is just slightly above the oil emulsification failure boundary, it was made sure that spherical structures are present. There will be four different contrast discussed here. The first contrast (Figure 1 left A) contained only protonated cyclohexane, resulting in a scattering length density of $1.7 \cdot 10^{10}$ cm^{-2} for an assumed homogeneous distribution. The radius of the micelle consists of the CO_2/cyclohexane mixture as well as of the amphiphilic film. In contrast to that, at the second contrast condition (Figure 1 left B) the radius of the micelle represents only the hydrophobic phase, as the scattering length density of brine was chosen to match the surfactants. Contrast C was aimed to minimize the scattering contribution of the structure and thus the scattering length densities of all components were chosen to be similar. The last contrast (Figure 1 left D) represents film contrast condition at which only the amphiphilic film contributes to the scattering intensity.

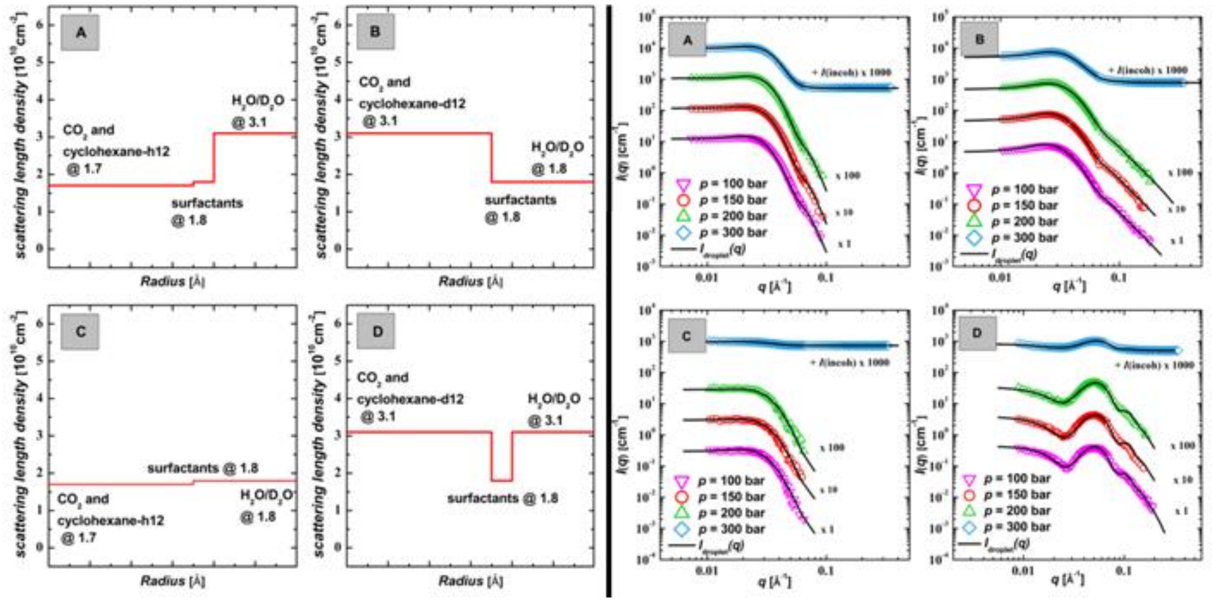

Figure 1: *Left:* 4 different contrast conditions which were chosen to investigate the distribution of CO_2 and cyclohexane within a micelle, which are shown here in a schematical way *Right:* Scattering curves for the four different contrast conditions. In all contrast conditions microemulsion droplets are present. The fitting functions represent a droplet form factor multiplied with the Percus-Yevick structure factor. The according fitting parameter are shown in Table 1.

The scattering curves for the four different contrasts explained in Figure 1 left are shown in Figure 1 right for four different pressures each. In all cases microemulsion droplets are present. The scattering curves have been described by a droplet form factor [4] and the Percus-Yevick structure factor [5] (black lines). The results of the fitting functions show (Table 1) that the radius of the droplets in contrast A and D are very similar, and that the ones in contrast B and C are smaller by about 4 Å which represents the thickness of the amphiphilic film. Interestingly, the Percus-Yevick structure factor is the same for all three contrasts, meaning that R_{PY} and σ_{PY} have the same values for each pressure in all different contrast conditions. As the structure factor describes interparticle contributions which are not affected by the contrast conditions this trends makes perfect sense.

Table 1: Parameters used for the fitting functions shown in Figure 1 right. In order to keep an overview only the parameters for p = 100 bar and 300 bar are shown as all trends are clearly visible within these data. Note that the structure factor parameters are the almost the same for all contrast conditions.

	p [bar]	R_0 [Å]	σ/R_0	d [Å]	χ [Å]	$\Delta\rho_{core}$ [10^{-6} Å^{-2}]	$\Delta\rho_{film}$ [10^{-6} Å^{-2}]	R_{HS} [Å]	σ_{HS}/R_{HS}
A	**100**	68	0.2	0.0	11	1.47	1.27	80.5	0.35
	300	59	0.18	12.0	8	1.20	1.27	75	0.32
B	**100**	62	0.23	10.8	1.5	-1.49	0.25	83	0.32
	300	54	0.25	10.7	1	-1.75	0.25	75	0.28
C	**100**	61	0.25	1.0	10	0.23	0.02	83	0.32
	300	54	0.25	12.0	9	0.26	0.02	75	0.32
D	**100**	65	0.14	12.5	3.8	-0.58	1.27	83	0.32
	300	59	0.16	13.0	3	-0.84	1.27	75	0.32

Generalized Indirect Fourier Transformation (GIFT): The scattering data shown in Figure 1 right were also analyzed applying the GIFT procedure which is a model-free way of describing scattering data. However, the description of interparticle interactions are not model-free which is why the Percus-Yevick structure factor for polydisperse spheres was taken into account at the calculations. The parameter chosen for the structure factor were the same, or at least very similar, as the ones described in Table 1. The first results of the GIFT procedure are the pair distance distribution functions (PDDF) which give information on the shape and the size of the particles. In a second step, the PDDF is deconvoluted to the scattering length density profile, using the program package DECON. The PDDFs and the according scattering length density profiles are shown in Figure 2.

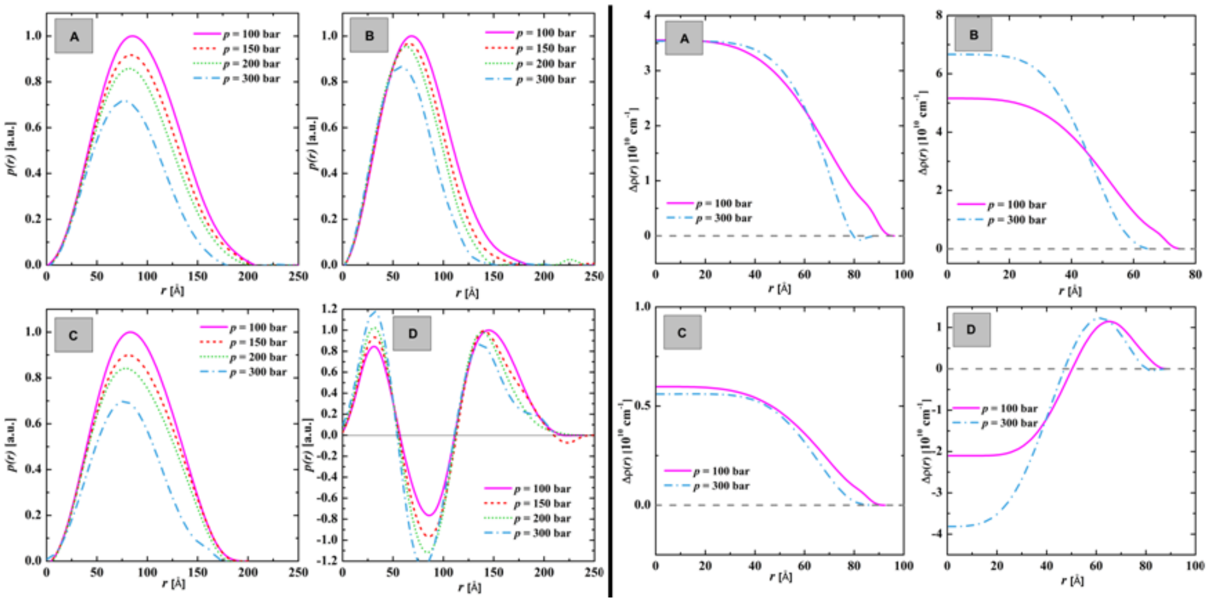

Figure 2: *Left:* Pair distance distribution function as calculated from the scattering curves. Contrast conditions A, B and C show a typical shape for spheres, only the PDDFs of contrast condition D are different which is probably due to multiple scattering contributions. *Right:* Scattering length density profiles deconvoluted from the PDDFs shown at the left hand side. Considering the scattering length density profile of contrast D, it becomes clear that the optimum film contrast condition was not achieved.

The PDDFs of contrast conditions A, B and C show a shape which is typical for spheres. The peak maximum gives information on the size of the sphere. Comparing the pressure-dependent PDDFs it becomes clear that the size of the micelles decreases with increasing pressure, which is in consistence with the information obtained from numerical fitting of the scattering curves. Only the PDDFs at contrast condition D show a shape which does not allow any information on the shape of the particle. The multiple peaks are probably a result of multiple scattering contributions, which arise of the fact that the perfect film contrast condition was not achieved, as indicated by both the SLD profile and the fitting parameters. Regarding the other contrast conditions, it is clearly visible that there is no sharp change of scattering length density from the hydrophobic phase to the hydrophilic phase, as has been previously reported [3], but that there is a transition within the micelle which expands over half of the droplet radius. Thus, we could clearly prove the existence of a depletion zone of cyclohexane within a micelle of a CO_2/cyclohexane mixture with fluorinated surfactants.

References:

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[2] Strey, R., Chalbi, A., Friederichs, W., Khazova, E., Kramer, L. G. A., Lindner, S., Posselt, V. and Sottmann, T. (**2009**), DE 102009053218A1.
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